THE NICKEL BULLETIN

A SUMMARY OF CURRENT INFORMATION ON NICKEL

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NOVEMBER, 1951

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VOLUME 24 **NUMBER 11**

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PHYSICAL AND MECHANICAL PROPERTIES OF MONEL

Monel is a nickel-copper alloy which has good mechanical properties and excellent corrosion-resistance to a wide range of substances. It can be used at moderately elevated temperatures and in sub-zero conditions.

Normal grades of Monel cannot be hardened by thermal treatment but mechanical properties can be enhanced by cold-working.

Typical Compositions, per cent.

	Wrought Monel	Cast Monel (Normal)	Cast Monel (2·75 Si)	Cast Monel (3·75 Si)
Nickel	67	63—68	63—68	63—68
Copper	Balance	Balance	Balance	Balance
Iron	1·40	3·0 max.	3·0 max.	3·0 max.
Manganese	1·00	0·5—1·5	0·5—1·5	0·5—1·5
Silicon	0·10	0·5—1·2	2·5—3·0	3·5—4·0
Carbon	0·15	0·30	0·12 max.	0·12 max.
Other Elements	S 0·01 max.	0·5 (inc. Mg 0·08-0·12 S 0·06 max.) Pb nil	0·5 (inc. Mg 0·08-0·12 S 0·05 max.) Pb nil	0·5 (inc. Mg 0·08-0·12 S 0·05 max.) Pb nil

Physical Properties

Lattice constant		3·541Å (face-centred lattice)
Specific gravity		8·83
Reflectivity	at 0·55μ	0·59

Electrical Properties

Specific Electrical Resistance		
microhms/cm./sq. cm.	0°C.	42·5
	20°C.	48
ohms/sq. mil. ft.	68°F.	228
Conductivity, per cent. (copper = 100)		4

Magnetic Properties*

Transformation Point °C.	43—60
Magnetic saturation value, *gauss*	1,000—2,000
Maximum permeability, *gauss*	2,000—10,000

Thermal Properties

Melting Range °C.	1,300—1,350
Latent Heat of Fusion, *cal./gram*	68
Specific Heat	
Mean 20°–400°C.	0·127

* Monel is only weakly magnetic. Cast Monel containing over 2·0% silicon is non-magnetic.

Thermal Conductivity, *c.g.s. units*

27–100°C.	0·062
200°C.	0·065
400°C.	0·074
600°C.	0·084
800°C.	0·094

Coefficient of Thermal Expansion, *millionths per deg. C.*

at 20°C.	12·8
100°C.	14·6
200°C.	16·0
300°C.	17·1
400°C.	18·2
500°C.	19·1

Average Coefficient of Thermal Expansion, *millionths per deg. C.*

0–100°C.	13
0–200°C.	14·3
0–300°C.	15
0–400°C.	15·8
0–500°C.	16·2

Moduli of Elasticity

millions of lb./sq. in.

In Tension	26
In Torsion	9·5
Poisson's Ratio	0·32

Mechanical Properties at Room Temperatures

Table I Typical Tensile Data

	Hot-Rolled Rod, Round, Square, Rectangle, Hexagon or Flat	Cold-Drawn Rod As-Rolled	Round, Square, Hexagon or Flat	Full Finish Sheet Normal	Cold-Rolled Sheet or Strip		Cold-Drawn Wire		Tubing		Castings		
					As-Rolled	Annealed	Normal	Annealed	As-Drawn	Annealed	Normal	2·75% Si	3·75% Si
0·2% Proof Stress, *tons/sq. in.*	20	36	15	22	42	12	60	15	40	13	11	18	—
Maximum Stress, *tons/sq. in.*	38	45	35	35	48	34	66	35	48	33	27	36	43
Elongation on $4\sqrt{\text{Area}}$, *per cent.*	35	20	45	30	12	45	8	45	15	35	25	12	Nil
Hardness, D.P.N.	150	220	140	145	230	135	—	—	—	—	125	200	260

Table II
Comparison of Strength in Shear and Tension

Condition	Soft	Half-Hard	Hard
Properties in Double Shear—			
Maximum Stress, *t.s.i.*	22	24	29
Deflection at Max. Stress	0·08	0·06	0·03
Tensile Properties—			
Maximum Stress, *t.s.i.*	31	34	52
Elongation in 2 in., *per cent.*	50	39	11·5
Hardness, D.P.N.	120	200	260

Table III
Comparison of Strength in Compression and Tension

	Hot-Rolled	Cold-Drawn[1]	Cold-Drawn[2] Annealed
Compression Data—			
0·1% Proof Stress, *t.s.i.*	15	26	8
0·2% Proof Stress, *t.s.i.*	17	36	12
Tensile Data—			
0·1% Proof Stress, *t.s.i.*	16	33	12
0·2% Proof Stress, *t.s.i.*	18	39	15
Maximum Stress, *t.s.i.*	37	43	35
Elongn. in 2 in., *per cent.*	39·5	27	44
Redn. of Area, *per cent.*	67·5	66·5	66
Hardness, D.P.N.	150	215	130

[1] All cold-drawn rods were given a 275°C. low-temperature, stress-equalizing treatment after cold-drawing.
[2] Three hours at 785°C., followed by furnace cooling.

Table IV Fatigue Limit and Apparent Corrosion-Fatigue Limits in Air, Fresh Water and Brackish Estuarine Waters

Condition	Annealed	Cold-Worked
Endurance Limit, 10^8 cycles, *tons/sq. in.*	16	22
Apparent Corrosion-Fatigue Limit 10^8 cycles, *tons/sq. in.*		
Fresh Water	9—11	9—11
Brackish Water	12—13	12—13

Table V Fatigue Properties of Sheet and Strip

Condition	Annealed	Full-Hard
Direction of Rolling with respect to length of specimen	Parallel	Parallel
Endurance Limit of 10^8 cycles, *tons/sq. in.*	11	17
Tensile Properties—		
Maximum Stress, *tons/sq. in.*	33	55
Limit of Proportionality, *t.s.i.*	9	26
Elongation in 2 in. *per cent.*	40·5	1·7
Endurance Ratio	0·333	0·309

Values were determined on sheet and strip and are minima obtained at 10^8 cycles of completely reversed stress.

Table VI Impact Strength

	Hot-Rolled	Forged	Cold-Drawn	Annealed
Impact Strength *ft./lb.*				
Izod*	100-120	75-115	75-115	90-120
Charpy*	220	—	150	215

* Determined with standard U-notch specimen: none of the specimens was fractured completely.

Mechanical Properties at High Temperatures

Table VII
Fatigue

Condition	Temperature °C.	Stress *tons/sq. in.*
Hot-rolled	540	±11
Cold-drawn	540	±12

NOTE.—The endurance limit at elevated temperatures is difficult to determine, but the above results of single tests may be of interest. They were carried out at a speed of 3,550 reversals per minute over 10^8 cycles.

Table VIII
Creep Strength

Condition	Temp. °C.	Stress (*tons/sq. in.*) to produce Creep Strain of	
		0·1% in 10,000 hr.	1·0% in 10,000 hr.
Hot-rolled	400	9	14
	430	7	10
	480	—	5
Cold-drawn, annealed 3 hours at 815°C.	400	9	13
	430	7	11
	480	3·5	7
	540	1·5	4

The tests were carried out on bars ½ to 1 in. diameter.

Mechanical Properties at Low Temperatures

Table IX
Mechanical Properties

Condition	Temperature °C.	Maximum Stress *tons/sq. in.*	0·2 per cent. Proof Stress, *tons/sq. in.*	Elongation in $4\sqrt{\text{Area}}$	Reduction of Area, *per cent.*
Cold-Drawn	Room	46	41	19·0	71·0
Cold-Drawn	−80	52	45	21·8	70·2
Cold-Drawn	Room*	46	41	17·3	72·5
Forged	20	41	30	31·0	72·7
	−180	57	41	44·5	71·8
	−250	63	43	38·5	61·0
Annealed	20	35	14	51·5	75·0
	−180	51	22	49·5	73·9

* Cooled to and held at −80°C. for several hours prior to testing at room temperature.

Table X
Charpy Impact Strength*

Temperature °C.	Impact Strength, *ft. lb.*	
	Hot-Rolled	Cold-Drawn Annealed
Room	220	215
−30	—	212
−80	213	219
−190	196	212

* Determined with standard W-notch specimen.

Table XI
British Standard Specifications for Monel

Hot-rolled sheet Cold-rolled sheet and strip	B.S. 1526 : 1949
Bars, rods and sections	B.S. 1529 : 1949
Tubes	B.S. 1532 : 1949
Wire	B.S. 1535 : 1949
Castings	B.S. 1537 : 1949

Table XII Fabricating Data

Stress Equalizing Cold-Worked Material	1 hr. at 275°C.
Stress Equalizing Hot-Worked Material	3 hr. at 575°C.
Soft Annealing Range	850°–950°C. (10–3 minutes)
Hot-Working Range	950–1150°C.
Pouring Temperature (Castings)	1540–1565°C.
Shrinkage Allowance on Patterns	¼ in. per ft.

ABSTRACTS OF CURRENT PUBLISHED INFORMATION ON NICKEL AND ITS ALLOYS

NICKEL

Centenary of the Discovery of Nickel

MOND NICKEL CO., LTD.: 'Axel Fredrik Cronstedt: The Man who Discovered Nickel.'
Publn. 553, 1951; 8 pp.

This is a biographical account of Cronstedt, placing emphasis on the primitive conditions in which the scientists of his period had to work, and the credit which should be given for discoveries made in such circumstances. In connexion with the centenary of Cronstedt's isolation of nickel, a scale model of his laboratory, based on information from contemporary records, has been constructed. A photograph of this model is reproduced in the publication.

Nickel: Sources, Supplies, Properties and Uses

J. V. BEALL: 'Nickel. A Journal of Metals Industry Report on Strategic Materials.' *Jnl. of Metals*, 1951, vol. 3, Sept., pp. 712-19.

A comprehensive survey, including tabular statistical information on world sources of nickel and the types of ore from which the metal is obtained; the metal content of the ores in the respective fields, and the estimated reserves; companies operating in the various localities and their processing facilities; current and future supply. Major uses of nickel are reviewed, with indication of the properties which make the metal essential in certain applications. Some of the methods being used to conserve nickel are indicated, with particular reference to the use of boron-containing steels.

Nickel Supplies and Usage: International Materials Conference

'International Materials Conference.' *Metal Industry*, 1951, vol. 79, Sept. 14, p. 220.

This note is a brief summary of some of the main points from the report recently issued by the Joint Sub-Committee on Utilization of Manganese, Nickel, Cobalt, Tungsten and Molybdenum.

The agenda for the first meeting, held during the summer in the U.S.A., covered a review of existing specifications, and problems of substitution and limitations in the use of metals, with special reference to end uses, salvage, and the use of scrap, in the following main fields of use:—ferro-alloys; steels and cast irons of all types; non-ferrous alloys; catalysts and chemicals. Some of the conclusions and recommendations made with regard to nickel are noted below:—

It is anticipated that present production of nickel will be increased by over 30 per cent. by 1954, but in the immediate future supply will not be able to meet demand. In spite of this shortage, the Committee is of the opinion that, wherever it is technologically possible, nickel should be used to relieve the cobalt position.

Among the specific means of saving nickel to which attention is drawn in the report are the maximum possible use of economy steels (especially low triple-alloy and boron-treated types), reduction of the nickel content of stainless steels, and down-grading of non-ferrous nickel-containing alloys. The recent development of spheroidal-graphite cast iron is regarded as a valuable contribution towards economy in alloyed constructional materials.

The use of nickel-coated steel in place of nickel sheet in thermionic valves is also considered to be possible in some cases, and it is further suggested that some economy can be effected in the use of nickel, cobalt, tungsten and molybdenum in magnet alloys.

Further meetings of the Committee are foreshadowed, since its members consider that only a preliminary attack has at present been made on the problems involved in conservation and efficient use of the materials included in their survey.

Desulphurization of Nickel: Estimation of Sulphur in Nickel

O. WERNER: 'The Desulphurization of Nickel.' *Metall*, 1951, vol. 5, Aug. and Sept., pp. 323-8; 381-4.

A brief summary is made of the classic work of MERICA and WALTENBERG and of MASING and KOCH, on the influence of sulphur on nickel, and the treatment with magnesium to produce malleable nickel. This is followed by consideration of the processes which may be used for determination of sulphur in nickel, for control of malleability. A detailed account is given of procedure used in wet chemical methods and of a method of spectrographic determination of magnesium.

It is noted that hot malleability of nickel is deleteriously affected by sulphur contents as low as 0·005 per cent., due to the formation of a low-melting eutectic of nickel/nickel sulphide, which collects at the crystal boundaries. An adequate addition of magnesium transforms the sulphur into a harmless constituent (magnesium sulphide), and restores malleability.

With regard to methods of determining sulphur in nickel, it is pointed out that the chemical methods usually employed give *total* sulphur content, but do not differentiate between the various forms in which the sulphur is present, and therefore are not fully significant in relation to control of the sulphur content of nickel. The hydrogen-reduction process is to be preferred, as indicating only the amount of sulphur present as Ni_3S_2, not that contained as MgS. Spectrographic analysis, which has the further advantage of rapidity, also differentiates satisfactorily, by estimation of the magnesium present. Procedure for spectrographic determination of magnesium is described, also a semi-quantitative method for estimation of the magnesium content of nickel.

Reversible Effects in Magnetization of Nickel

R. S. TEBBLE, W. D. CORNER and J. E. WOOD: 'Reversible Effects in the Magnetization of Nickel.' *Proc. Physical Soc., Sect. B*, 1951, vol. 64, Sept. 1, pp. 753-60.

A report is made of investigations on the temperature dependence of the contribution from reversible processes to the magnetization of annealed and strained nickel wires. The measurements recorded relate to carbonyl nickel of the following composition: carbon 0·04, silicon 0·05, iron 0·15, manganese 0·03, aluminium 0·01, magnesium 0·13, sulphur 0·003, per cent., nickel balance. The composition approximates closely to that of nickel used by the senior author in investigations on the reversible susceptibility of ferromagnetic materials at room temperature (*ibid.*, 1950, vol. 63, p. 1005).

The work reported in the present paper involved measurement of reversible susceptibility k_r over a range of field and of temperature (−50°C. to 200°C.). A rapid method of recording $k_r - H$ curves was developed.

The effect of temperature on reversible susceptibility is discussed in relation to Becker's strain theory: reasons for discrepancies are suggested. It is shown that the contribution of reversible processes to the total change in magnetization, integrated over the hysteresis cycle, increases with temperature and strain, from 15 per cent. for an annealed specimen at −50°C. to 85 per cent. for a strained specimen at 150°C. The effect is not uniform over the whole cycle, and in the region of the coercive field a considerable part of the change in magnetization is attributed to irreversible processes.

Domain Structure in Nickel Single Crystals

H. J. WILLIAMS and J. G. WALKER: 'Domain Patterns on Nickel.' *Physical Rev.*, 1951, vol. 83, Aug. 1, pp. 634-6.

Domain patterns were observed on two single crystals of nickel cut in the form of hollow parallelograms. The length of the sides was parallel to the (111) directions in the one specimen, and to the (110) directions in the other. The crystals showed domain structures with the three types of domain boundaries which are to be expected from a material having the directions of easy magnetization along the (111) directions. Domain-boundary movement under the influence of an applied magnetic field was observed. Attention is directed to earlier work on nickel by BITTER, and by MCKEEHAN and ELMORE, with which the present authors' observations are not in agreement.

British Specifications for High-Nickel Alloys

See abstract on p. 241.

Nickel for Thermionic Valves

A. M. BOUNDS and T. H. BRIGGS: 'Nickel Alloys for Oxide-Coated Cathodes.' *Proc. Inst. Radio Engineers*, 1951, vol. 39, July, pp. 788-99.

The authors have been intimately associated with recent investigations carried out, under the auspices of the American Society for Testing Materials, on materials for thermionic valves.

Part I of the paper outlines some of the essential features of valves of this type, as a background to consideration of the materials to be used and the properties required in them.

Part II describes methods used for extraction and refining of the nickel used: typical (1947) compositions of electrolytic and carbonyl nickel are given. Production of the necessary malleability in nickel is discussed in relation to the residual elements which must be present, and the influence of such elements is in turn considered as affecting the thermionic emission of the nickel-base cathode. The influence of magnesium, titanium, boron, manganese, iron, copper, and silicon calls for attention in this connexion.

This section also contains a description of fabricating operations standard for production of the seamless tube and the strip for seamed cathodes used in the valves. These operations, provided that they are correctly controlled, are believed to have little effect on cathode characteristics, but slight change of composition may be introduced by oxidation, contact with steel tools, and heat-treatments in 'special' atmospheres. The rôle of reducing elements is then discussed from the metallurgical standpoint, with particular reference to the very general opinion that magnesium, silicon and other elements which can reduce the coatings are the primary source of emissive activity.

Part III deals with oxide-coated cathodes, and the inter-relation of coating and cathode material, as affecting service behaviour. The importance of continuous regeneration of the surface barium layer of the coating is emphasized, and the function of the reducing action of certain elements in the cathode base metal is indicated. The most important alloy reducing agents currently used are magnesium, aluminium, silicon, tungsten and carbon: in reacting with barium oxide they produce compounds at the core-coating interface. Some typical oxide-cathode reactions are discussed, and their effect on tube behaviour.

Part IV. With the foregoing discussion as background, the authors consider, seriatim, the effects of each of the common additive elements which may be present in nickel-base cathode alloys: (*a*) *reducing agents* (magnesium, aluminium, silicon, titanium, tungsten, carbon, and cobalt), and (2) *other elements* (chromium, copper, iron, manganese, lead, tin, and zinc).

Table I (p. 229) gives the composition of U.S. commercial cathode alloys currently on the market.

A critical consideration of these compositions and of the materials now used in other countries for this purpose leads the authors to the conclusion that most of them are far from being ideal. *Inter alia*, higher strength is required, for tubes called upon to operate in mechanically severe conditions: for this purpose additions of tungsten, cobalt and molybdenum, combined with additional mechanical processing, are considered promising. Recent advances in the knowledge of cathode behaviour have provided information on which it is believed improved cathode materials can be developed. It is suggested that four alloys of three grades (see Table II on p. 229) would, for some time to

Table I

Composition of U.S. Commercial Cathode Alloys
(Maximum per cent., by weight, unless range is shown)

A.S.T.M. Grade	Cu %	Fe %	Mn %	Mg %	Si %	Ti %
Active-Alloy Type						
1	0·20	0·20	0·20	0·01—0·10	0·12—0·20	0·02
2	0·04	0·10	0·05	0·01—0·10	0·12—0·20	0·01
3	0·20	0·20	0·20	NS	0·15—0·25	NS
4	0·04	0·05—0·10	0·10	0·01	0·15—0·25	NS
5	0·04	0·05—0·10	0·10	0·05—0·15	0·05—0·15	NS
6	0·04	0·05	0·02	0·01	0·15—0·25	NS
Normal-Alloy Type						
11	0·02	0·02	0·02	0·01—0·10	0·01—0·05	NS
Passive-Alloy Type						
21	0·04	0·05	0·02	0·01	0·01	NS

NS = Not Specified. Normally: S < 0·005 per cent. C = 0·01 per cent. per 0·001 in. thickness of nickel sleeve wall.

Table II

Alloy and Grade	Aluminium %	Magnesium %	Silicon %	Tungsten %
Active-Premium	0·03 max.	0·02—0·07	0·03 max.	3·75—4·25
Active-Commercial	0·03—0·10	0·02—0·07	0·05 max.	—
Normal	0·02 max.	0·02—0·07	0·02—0·06	—
Passive	0·01 max.	0·01 max.	0·01 max.	—

Carbon should average about 0·02 per cent. per 0·001 in. of strip or wall thickness.
The alloys should have uniformly low levels of impurity content, e.g., of copper, iron, manganese and titanium.

come, satisfy the needs of the radio-receiving-tube industry.

Such alloys would have low rates of sublimation and low interface-impedance values. They would provide three levels of saturated emission (both d.c. and pulsed) and three levels of rate of free barium evolution. Their rates of activation could be controlled by tube-exhaust and processing schedules. Any alloys selected must be such as can be produced under commercial conditions, and must be closely reproducible. These requirements, it is believed, could be met by the alloys proposed.

Separation of Nickel from Other Metals by Chromatographic Analysis

J. A. LEWIS and J. M. GRIFFITHS: 'Inorganic Chromatography of Cellulose. Part IV. Determination of Inorganic Compounds by Paper-Strip Separation and Polarography.' *Analyst*, 1951, vol. 76, July, pp. 388-95; disc., p. 395.

In the method described, separation is performed by placing an accurately measured volume of the test solution near one end of a strip of absorbent paper. The end of the strip nearest the test patch is then immersed in the organic solvent, which is allowed to diffuse through the paper and over the sample of metal salts. One or more of the metal salts dissolves and moves down the paper, to form well-defined zones. The regions containing the metal salts are then separated from the rest of the paper strip and the amount of metal in each region, after solution, is determined by the polarograph.

Three types of separation are described, (1) separation of one metal from a mixture, exemplified by uranium in the presence of a large number of other metals, (2) separation of several metal salts in a mixture, such as cobalt, nickel and copper in a sample of alloy steel, and copper and cobalt in iron pyrites, and (3) separation of a mixture of metals into groups containing several metals that can be determined by polarography without further separation, represented by ten metals separable into two groups of five containing (i) vanadium, copper, uranium, lead and titanium, and (ii) iron, molybdenum, bismuth, antimony and cadmium.

A new supporting electrolyte for use in polarography is described. This makes use of salicylic acid, to form complex ions with certain metals; the procedure has been found valuable for determination of several metals in a mixture.

Brazing and Soldering of Nickel, Monel and Inconel

See abstract on p. 235.

Bonding of Titanium Carbide with Nickel

See abstract on p. 244.

Carbonyl Nickel as Catalyst

L. L. BAKER and R. B. BERNSTEIN: 'Carbonyl Nickel Films as Hydrogenation Catalysts.' *Jnl. Amer. Chemical Soc.*, 1951, vol. 73, Sept., pp. 4434-6.

Although nickel carbonyl has been used as a catalyst for various reactions (see, for example *Bull. Soc. Chim. France*, 1948, p. 529) the catalytic properties of nickel deposited viâ the carbonyl have not, so far as the authors are aware, been previously investigated.

This paper describes experiments in which it was demonstrated that thin films deposited by decomposition of nickel carbonyl, on Pyrex glass, were active hydrogenation catalysts. Films having a nominal thickness of 0·1 μ were satisfactory catalysts for the reaction of hydrogen with propylene. Small quantities of carbonyl nickel were readily prepared, using a static decomposition method, and a continuous-flow process was found suitable for obtaining large amounts of catalyst. Several series of experiments were carried out with catalysts formed on Pyrex wool at 150°C., employing about 90 mg. of nickel, as well as thin films (ca. 4 mg.) deposited directly on the walls of a Pyrex vessel. For equimolar mixtures of hydrogen and propylene at 37° and 80°C., the rate of the reaction could be expressed accurately by the equation: $-dp/dt = kp^2/(1+Kp)^2$, where p is the partial pressure of either reactant. This finding is considered to suggest that the operative mechanism is competitive adsorption of both reactants, without interference from the product. The films proved to be appreciably susceptible to poisoning by a substance of undetermined identity.

The carbonyl-nickel catalysts may easily be prepared in the quantity desired. Since the surface is initially free of hydrogen, such material would appear to be especially well suited for investigations concerned with addition, isomerization and exchange reactions of hydrocarbons using deuterium or tritium.

Nickel-Copper Catalysts

See abstract on p. 232.

Nickel-, Inconel- and Stainless Steel-Clad Molybdenum for High-Temperature Service

See abstract on p. 244.

ELECTRODEPOSITION AND OTHER COATING METHODS

Electrodeposition of Nickel with Insoluble Anodes

W. A. WESLEY, D. S. CARR and E. J. ROEHL: 'Nickel Plating with Insoluble Electrodes.' *Steel*, 1951, vol.129, Sept. 10, pp. 112, 114. (Short abstract of paper to Amer. Electroplaters' Soc.)

Electrodeposition of nickel with insoluble anodes offers advantages in certain applications, such as plating of steel strip or wire, rolls, or the interior of tubes, or for electroforming. The main obstacle to the use of the process has hitherto been the difficulty of replenishing the nickel content of the bath economically and with good control.

This problem has been solved by the method described in the present paper, which involves continuous replenishment by circulation of the electrolyte through a plating tank, a regeneration tank, and a filter. In the regeneration tank nickel is dissolved at a controlled rate with the aid of periodic reversal of current, and the pH of the solution increases. In the plating tank the nickel content is depleted and the pH decreases. Provided that the electrode area in the regeneration tank is adequate, composition and pH of the electrolyte can be controlled simply by adjustment of the current in that tank. Power costs for the regeneration cell are low, because it can be operated with close electrode spacing, low current density and a series-parallel electrode arrangement.

Hardness and tensile strength of deposits made from the chloride-free bath described are slightly higher than those obtained from a Watts-type bath: ductility is somewhat lower.

Problems of ventilation are discussed, as arising from the fact that, in the process described, copious quantities of gas are liberated at the electrodes, and give rise to considerable spray.

The essential features of the method are covered by *U.S. Patent 2,541,721:* see *Nickel Bulletin*, 1951, vol. 24, Nos. 9-10, p. 219.

Influence of Ultrasonics in Electrodeposition of Nickel

A. ROLL: 'The Effect of Ultrasonics in Electrolytic Processes. IV. Effect of Ultrasonics on Bright-Nickel Plating.' *Zeitsch. für Metallkunde*, 1951, vol. 42, Aug., pp. 238-43.

The author reports experiments made to demonstrate the effect of ultrasonic irradiation on the surface condition of electrodeposited nickel. The field was applied parallel to the cathode.

The current densities over which bright deposits can be obtained are shifted to higher values as the intensity of the ultrasonic irradiation is increased. In presence of an ultrasonic field the metal ions travelling towards cathode are subjected to an influence producing oscillatory movement; this is superimposed on the migration velocity. As a result the ions do not impinge at right angles on to the cathode, but at a certain angle.

Experimental observation has shown that in the bright-plating range this angle is very large, but that if the angle of striking is smaller than is critically optimum for brightness a crystalline deposit is formed. If it is greater than the critical optimum, uneven but bright deposits are still formed; these are observed only when deposition is done under the influence of ultrasonic irradiation.

In view of the complexity of the deposition mechanism it is not very probable that the occurrence of bright deposits can be explained solely by such a simple mechanism. Since, however, the influence of an ultrasonic field can be unequivocally explained by such an assumption, other known facts with regard to electrodeposition of metals are discussed from that standpoint, and it is found that the presumption is not in any way contradictory of other facts established with regard to deposition of bright coatings. It is therefore concluded that physical quantities, expressible in terms of the angle of impingement, are an important factor in production of bright deposits.

Thickness Testing of Electrodeposited Coatings

H. J. READ and F. R. LORENZ: 'Methods for Testing Thickness of Electrodeposits. III. Comparison of Methods for Acid Copper on Steel.' *Plating*, 1951, vol. 38, Sept., pp. 945-52, 958.

Report issued under the aegis of A.E.S. Research Project 7.

The preceding paper in this series dealt with thickness measurements of nickel deposits on steel (*ibid.*, 1951, vol. 38, pp. 255-63: *Nickel Bulletin*, 1951, vol. 24, No. 5, p. 100).

Copper coatings on steel present a magnetic condition entirely different from that involved in nickel on steel, since in the case of the copper coatings only the basis metal is magnetic. This simpler magnetic system permitted the use of two additional tests, not suitable for the earlier investigation, viz., (1) the General Electric thickness gauge, and (2) the Lea Lectromag. All the methods used on the nickel coatings were also used on the copper-coated specimens. Nominal thicknesses of coatings used were 0·0001, 0·0005, 0·001, 0·0025 and 0·005 in. (2·5, 13, 25, 65 and 130μ).

The conclusions drawn from the tests (full details of which are recorded) are given below:—

The reproducibility of the Magne-gage, G.E. thickness gauge, Lectromag, B.N.F. jet test, microscopic method and stripping method is acceptable for most purposes, except when the microscopic method, the G.E. gauge and the B.N.F. test are used on thicknesses below 0·0005 in. (13μ). The B.N.F. jet test is also unsatisfactory for thicknesses of 0·0025 in. (63μ) or above.

Effect of Contaminants in Nickel-Dip Treatment

J. M. ZANDER and O. C. LINHART: 'Effect of Ferrous and Sodium Sulphate on the Rate of Nickel Deposition.' *Better Enameling*, 1951, vol. 22, May, pp. 6-7.

The authors report an investigation of inconsistencies observed in adherence of enamel coatings deposited on ware which had been prepared by nickel-dip treatment. The success of this treatment is dependent, to a large extent, on the amount of nickel deposited, and it was desired to ascertain whether contamination of the plating bath could occur to a degree which would reduce the nickel film to an inadequate thickness.

Ferrous sulphate is the immediate chemical end-product contaminant formed in a nickel solution by the galvanic displacement of iron for nickel, when iron ware is immersed in the bath. The amount of iron entering into solution is dependent on the area of work put through the solution and the average weight of nickel deposited per square foot of ware, but the actual concentration of ferrous sulphate present in the bath at any given moment varies not only with these factors, but also with the rate at which the iron tends to hydrolyze out of solution, and the extent of drag-out under operating conditions.

At a pH of 3-4, and at the elevated temperatures at which the nickel-dip bath is usually worked, ferrous sulphate is comparatively stable, and no appreciable precipitation of iron occurs until some of the iron salts in solution are oxidized, either by the oxygen dissolved in the bath or by air, to the ferric state. In this form the iron, through hydrolysis on heating, is removed from the solution as a highly coloured precipitate, and this chemical change is associated with gradual lowering of the pH of the solution.

Under normal plant conditions, conversion of ferrous to ferric iron, by oxidation, is not very rapid, and precipitation of the iron is never complete, due to constantly changing chemical equilibrium conditions. By comparison with the actual concentration of ferrous sulphate, only a relatively small amount of ferric iron is continuously removed, and the ferrous-sulphate content of the bath consequently gradually builds up.

In order to determine the effect of such increasing ferrous-sulphate concentration, on deposition of nickel, test plates were prepared according to standard procedure and were immersed for five minutes in a solution containing 2 oz. of single nickel salts per gallon, to which ferrous-sulphate additions were made over the range 0·05 to 3·30 per cent. The bath was operated, in all cases, at 165°F. (74°C.), and a pH of 3·2. The results obtained established a definite trend of decrease in deposition of nickel with increasing ferrous-sulphate content.

A further series of experiments was made to estimate the possible influence of sodium sulphate, which may considerably increase from additions of caustic made to neutralize excess acidity and maintain a pH of 3-4. The mode of procedure was similar to that adopted in the ferrous-sulphate tests, and in this case also definite reduction in the amount of nickel deposited was observed in relation to increase in contamination.

It is pointed out that, under existing conditions of shortage of nickel, some enamellers are attempting to conserve nickel by operating plating baths beyond their normal life. This has been done by periodic removal of ferrous sulphate (see method described in *Better Enameling*, Dec., 1950). This procedure, however, involves use of sodium sulphate in amounts

far in excess of the quantity which would be used to restore the pH to the 3-4 level, and it is therefore probable that removal of ferrous sulphate has resulted, in many cases, in build-up of sodium sulphate to an extent which seriously reduces the rate of deposition of nickel.

Nickel Salts in Gold-Alloy Plating Solutions

E. R. THEWS: 'The Production of Colored Gold Finishes.' *Metal Finishing*, 1951, vol. 49, Sept., pp. 80-5.

The article contains a discussion of the various factors involved in electrodeposition of coloured gold and gold-alloy deposits. Details are given of the composition of the solutions used for deposition of gold of various carats, and of baths for production of green, pink and rose, and white gold plating. Nickel cyanide is an integral constituent of many of the solutions described. The influence of temperature, current density and other variables is considered, and heat-treatment and diffusion processes which may be applied to the electrodeposited coatings are reviewed.

NON-FERROUS ALLOYS

Nickel-Copper Catalysts

N. KADOTA and S. IKEDA: 'X-ray Diffraction Study on the Structure of the Ni-Cu Coprecipitation Catalysts.' *Jnl. Amer. Chemical Soc.*, 1951, vol. 73, Sept., pp. 4475-6.

Reports of the influence of copper on the activity of nickel catalysts are contradictory: both inhibitor and promoter action has been found, e.g., in the Fischer-Tropsch process copper acts as an inhibitor, whereas in ordinary hydrogenation it may be used to promote the activity of nickel.

Study of the co-precipitation of nickel and copper (MORRIS and SELWOOD, *ibid.*, 1943, vol. 65, p. 2245: *Nickel Bulletin*, 1944, vol. 17, No. 1, p. 18) suggested the possibility of the existence of a non-equilibrium alloy phase. The present authors, on examination of the structure of nickel-copper catalysts co-precipitated from their nitrate solutions, on kieselguhr, confirm the findings of Morris and Selwood. A non-equilibrium state of the alloy is formed on the catalyst surface and remains unstable there to an extent depending on the composition of the catalyst.

Properties and Uses of Nickel-Aluminium Bronzes

J. S. VANICK: 'Nickel-Aluminium Bronze.' *Foundry*, 1951, vol. 79, Aug., pp. 98-102; Sept., pp. 108-11, 192, 195.

These articles comprise a detailed account of the composition, properties and uses of copper-base alloys containing aluminium of the order of 8-10·5 per cent., with varying amounts of nickel.

Reference is directed to the standard U.S. and British specifications (respectively, A.S.T.M. B-148:49 and B.S. 1400-AB2-C), and the physical and mechanical properties of alloys falling within the limits set by these specifications are tabulated and discussed. The rôle of nickel in such alloys is considered:—grain-refinement, and improvement of hardening qualities, mechanical strength, and physical properties. The corrosion-resistance of the nickel-aluminium bronzes is also of a high order, and their ability to withstand cavitation-erosion is utilized to advantage in pumps and propellers. Test data recorded in the paper show that under conditions involving contact with rapidly moving sea water a high-strength nickel-aluminium bronze (nickel 5·5, aluminium 10, iron 4, per cent.) is most suitable, while in contact with slowly moving or stagnant sea water aluminium bronzes containing less than 10 per cent. of aluminium, with 2½-5 per cent. nickel and no iron are to be preferred.

Nickel-aluminium bronzes retain a high proportion of their mechanical strength at temperatures up to about 750°F. (400°C.), a characteristic which, coupled with their good resistance to corrosion and oxidation, makes them suitable for service in steam plant, i.c. engines and some chemical-engineering applications. Short-time tensile tests on sand-cast bars at temperatures up to 930°F. (500°C.) are recorded in the paper, together with creep tests at 500°F. (260°C.). Due to the tenacious self-healing oxide film which tends to form on these alloys, they are used in certain high-temperature applications, e.g., as moulds, dies, neck rings and plungers in glass manufacture. Higher-nickel grades of aluminium bronze also find application in this connexion, e.g., an alloy containing copper 62, aluminium 7, nickel 22, zinc 7, per cent. Commercial specifications for this type of material place a 1 per cent. maximum on iron and 0·25 per cent. on lead.

The high hardness and strength of the 10/4/2·5 per cent. aluminium-iron-nickel alloy (grade 9C of the A.S.T.M. specification) make possible its use for wear-resisting applications, especially those involving dry running, or actual abrasion. The retention of hardness at elevated temperatures is a useful feature in this type of service.

Aluminium bronzes having a Brinell hardness of the order of 200 possess machining characteristics resembling those of mild steel. Where specially high machinability is essential lead may be introduced, but the presence of lead vitiates response to heat-treatment and is deleterious also in some other respects. Lead should be used with caution.

Nickel-aluminium bronzes can readily be welded, brazed, and hard- and soft-soldered. Difficulties at one time encountered in soft-soldering have been overcome by use of orthophosphoric acid as a flux.

The nickel-aluminium bronzes resemble steels in their response to heat-treatment, and the influence of nickel is closely similar in the two cases: its effect is to slow down transformation and stabilize structure: the mechanical properties of nickel-containing aluminium bronzes may be varied over a relatively wide range by suitable heat-treatment conditions. A typical treatment for the 5 nickel, 5 iron, 10 aluminium alloy would consist in heating the casting at 1600°–1650°F. (870°–900°C.) for 1–3 hours, quenching, tempering for 1–3 hours at 1100°–1150°F. (530°–620°C.), and again quenching. Properties typical of this alloy in the as-cast and the heat-treated conditions are shown

Table I

Condition	Ultimate Tensile Strength		Yield Strength		Elongation	Reduction of Area	Brinell Hardness
	p.s.i.	t.s.i.*	p.s.i.	t.s.i.*	%	%	
Sand-Cast	95,000	42·5	45,000	20·0	7	7	195
Heat-Treated	115,000	51·5	70,000	31·5	5	6	235

* To nearest half ton.

in Table I above.

Modification of this heat-treatment (higher quenching temperatures or lower tempering temperatures), may be applied to develop higher hardness. Softening may be achieved by raising the tempering temperature or the time of treatment. It is considered that much work still requires to be done to establish fully the potential value of heat-treatment for these alloys, with particular reference to the modifications obtainable by precipitation-hardening.

The final section of this article reviews some typical applications of the nickel-aluminium bronzes: these are noted below:—

Aircraft parts: propeller hub bushings and bearings, and fastenings; valve guides and valve seats.

Dies and Gears: dies, forming tools and fixtures, in which good hardness and low frictional drag can be secured: rolling-mill screw-down nuts, washers, slippers, etc.

Marine Engineering: ships' propellers, in which the cavitation-resisting qualities of the alloys are utilized; rudders, propeller caps and stern tube bearings are further applications, also various types of marine valve.

Power Plant: steam valves, pumps and accessories, combining the advantages of strength at elevated temperatures with high hardness and resistance to corrosion.

Electrical Equipment: welding-electrode holders, holders for electric motor brushes, transformer fittings, and certain types of switchgear, applications in which use is made of the almost non-magnetic character of the material, combined with its hardness and high strength.

Chemical Plant and Equipment: in various branches of this industry, e.g., paper, textile and petroleum plant, the corrosion-resisting qualities of the nickel-aluminium bronzes are of advantage, considered in conjunction with their physical and mechanical properties. In comparison with other copper-base alloys they give better resistance to gases containing sulphur dioxide, hydrogen sulphide, or low concentrations of oxidizing acids.

Hydro-electric and Water Works: flood-control valves, pumps and hydro-electric control mechanisms represent current applications, also stems, valves, guides and gates for valves; pump impellers and housings.

Nickel-aluminium bronze castings in the lower-alloy range are being regularly made by permanent-mould processes, and vacuum-cast alloys of nickel-aluminium bronze are in daily production for hundreds of small castings. Mechanical properties and typical compositions of such alloys are shown below:

Table II

Cu	Al	Fe	Ni	Others	Ultimate Tensile Strength		Yield Strength		Elongation in 2 in.	Hardness, Rockwell 'B'
%	%	%	%	%	p.s.i.	t.s.i.*	p.s.i.	t.s.i.*		
80·5	10·5	4·25	4·75	0·5 max.	90,000	40·0	50,000	22·5	10	89
					100,000	44·5	60,000	27·0	5	93
76·0	12·0	5·0	7·0	0·5 max.	105,000	47·0	80,000	36·0	5	100
					120,000	53·5	85,000	38·0	0	110

* To nearest half ton.

British Specifications for High-Nickel Alloys

See abstract on p. 241.

Constitution of Nickel-Manganese Alloys

B. R. COLES and W. HUME-ROTHERY: 'The Equilibrium Diagram of the System Nickel-Manganese.'

Jnl. Inst. Metals, 1951-52, vol. 80, pp. 85-92: Advance Copy 1327: *Monthly Jnl.*, Sept., 1951.

The investigation was mainly concerned with determination of the equilibrium diagram of the nickel-manganese system at temperatures above 800°C.: some information was also obtained on structures existing at lower temperatures. A combination of thermal, microscopical and X-ray methods was used.

It was found that the liquidus and solidus pass through a smooth minimum at 62 at. per cent. manganese, at 1018°C. Nickel is freely soluble in γ-manganese, and nickel additions increase the axial ratio of the face-centred-tetragonal structure until it becomes cubic and unites with the solid solution of

manganese in nickel. Immediately below the solidus there is therefore a complete range of solid solution extending across the diagram.

At lower temperature (ca. 910°C.) this solid solution in the equi-atomic region is transformed into a β phase, having a body-centred-cubic structure which cannot be retained by quenching.

At a still lower temperature the β phase is transformed into a phase having a face-centred-tetragonal superlattice of the CuAu type. The temperature of the $\delta \rightleftarrows \gamma$ transformation of manganese is raised by addition of nickel, whereas the temperatures of the $\gamma \rightleftarrows \beta$ and $\beta \rightleftarrows \alpha$ transformation are lowered.

The nickel-manganese diagram in some respects resembles that of the nickel-zinc system, suggesting that manganese acts as a divalent element in some of the allovs.

Structure of Nickel-Manganese Alloys

B. L. AVERBACH: 'X-Ray Detection of Long-Range Order in Ni_3Mn.' *Jnl. Applied Physics*, 1951, vol. 22, Aug., pp. 1088-9.

Record of observations on a binary alloy containing 25·5 at. per cent. manganese.

The ingot was homogenized at 1000°C., quenched, and cold-reduced 94 per cent. to 1·5 mm. wire. The specimen was ordered by heating to 600°C. and cooling at 20°C. per hour in the range 600°C.-500°C. and at 20°C. per day from 500°C. to 300°C. Recrystallization also occurred as a result of this treatment and the grain size of the wire was sufficiently fine to produce smooth X-ray-diffraction lines. After the ordering treatment the diameter of the wire was reduced to 0·5 mm. by electropolishing.

A microphotometer trace of a film produced by a 72-hour exposure, under conditions described, indicates clear visibility of the superstructure lines (110), (210), (211) and the combination (300) and (221). The (100) line could be seen, and its position on the film determined, but it was too weak to be recorded by the microphotometer. The superstructure lines are consistent with a Cu_3Au ordered structure and a lattice parameter of approximately 3·59 Å referred to the disordered f.c.c. structure. Degree of order is now being measured as a function of temperature.

The work is being carried out under contract for the Atomic Energy Commission.

Structure of Nickel-Gold Alloys

P. A. FLINN and B. L. AVERBACH: 'Atomic Arrangement in Gold-Nickel Solid Solutions.' *Physical Rev.*, 1951, vol. 83, Sept., p. 1070.

Measurements of diffuse X-ray scattering from gold-nickel solid solutions have given results which differ markedly from the predictions of simple statistical theory. This system shows a continuous solid solubility in a face-centred-cubic lattice above 840°C.: below this temperature two other face-centred-cubic lattices, one rich in nickel and the other in gold, co-exist. Above 840°C., therefore, the solid solution would be expected to contain nickel-rich and gold-rich clusters, which would act as nuclei for subsequent precipitation.

The diffuse scattering to be expected from a nickel-gold solid solution containing clusters has been calculated, but the experimental results reported in this note do not conform to expectation, and it is concluded from the data obtained (on alloys containing 10–90 per cent. gold) that there is no clustering of like atoms in these solid solutions. Elucidation of the exact atomic arrangement awaits closer interpretation of the diffuse X-ray scattering observed, and further experiments, on single crystals of the alloys.

Structure of Nickel Silicide

K. TOMAN: 'The Structure of NiSi.'
Acta Crystallographica, 1951, vol. 4, Sept., pp. 462-4.

The structure of NiSi was determined from Weissenberg and rotating-crystal photographs, using $CuK\alpha$ radiation. Dimensions of the unit cell, determined by the powder method, are given as $a=5·62$, $b=5·18$, $c=3·34$ Å. The space group is *Pbnm* and there are four molecules in the unit cell. The structure is a deformed NiAs arrangement.

Determination of Cobalt in Nickel-containing Materials

J. A. DEAN: 'Isolation and Determination of Cobalt.' *Analytical Chemistry*, 1951, vol. 23, Aug., pp. 1096-7.

The sulphonated portion of certain organic reagents has been found to enter readily into anion-exchange reactions, on a column of acid-washed alumina, without impairing the ability of the chelate groups to form complexes with metals. Only the surfaces of the alumina particles are covered, instead of having an entire column packed with the organic reagent.

Nitroso-R salt was first tried and it is with the results of such tests that this paper is concerned. It was found that the sulphonic-acid groups attached to the molecule are readily adsorbed on a perchloric-acid-washed alumina column, without disturbing the ability of the α-nitroso-β-hydroxyl groups to form an inner complex salt with cobalt. The brilliant red colour of the cobalt complex is developed in the usual manner (see *Analyst*, 1942, vol. 67, p. 97), and, following the acidification step, the solution is passed through the alumina column, during which operation only the cobalt complex and excess unreacted nitroso-R salt are adsorbed. Successive elution, first of the excess reagent with hot 1*M* nitric acid, and then of the coloured complex with 1*M* sulphuric acid, enables the cobalt complex to be isolated and its transmittancy to be subsequently measured. The entire procedure requires only about 20 minutes after dissolution of the sample.

By comparison with methods previously used for estimation of small amounts of cobalt, the chromatographic ion-exchange modification renders the nitroso-R salt a specific reagent for cobalt, and eliminates the necessity for removal of copper, chromium and appreciable quantities of iron; it also overcomes interference by nickel. The procedure has been successfully applied to analysis of a wide variety of steels, including stainless nickel-containing types, and to copper- and nickel-base alloys. Results obtained on a number of Bureau of Standards samples are tabulated:

these include determination of cobalt in 36 per cent. nickel steel, high-alloy cast iron, chromium-nickel-iron alloys and stainless steels, copper-nickel-zinc alloy and a 66-29 per cent. nickel-copper alloy.

Brazing and Soldering of Nickel, Monel and Inconel

INTERNATIONAL NICKEL CO., INC.: 'Brazing and Soldering Nickel and High-Nickel Alloys.' *Tech. Bull. T*-34,* Aug., 1951; 17 pp.

A well-illustrated manual of recommended procedure, covering methods suitable for Monel and K Monel, nickel (wrought, and low-carbon types), Duranickel, Inconel, Inconel 'X' and Inconel 'W'.

Design, brazing materials, surface preparation, methods of heating, and post-brazing treatment are discussed, as related to silver brazing and copper brazing. Special consideration is given to conditions required in brazing parts which are to be used in high-temperature service, and attention is directed to brazing alloys which have been specially developed for such use, e.g., Nicrobraz (nickel 65-75, chromium 13-20, boron 2·75-4·75 per cent., with iron, silicon and carbon limited to 10 per cent. max.).

The final section of the publication reviews factors involved in soft-soldering of nickel-base materials. Design of joints for soft-soldering is discussed, with illustrations of suitable forms, the compositions of typical soft solders are tabulated, and information is given on fluxes for this type of work. Methods of heating, and post-soldering treatments are also considered.

* *We shall be pleased to supply a free copy of this publication.*

NICKEL-IRON ALLOYS

Martensitic Transformations in Nickel-Iron Alloys

E. S. MACHLIN and M. COHEN: 'Burst Phenomenon in the Martensitic Transformation.' *Jnl. of Metals*, 1951, vol. 3, Sept. (*Trans. Amer. Inst. Mining and Metallurgical Engineers*), pp. 746-54: T.P. 3127E.

In an investigation of the martensitic habit in single crystals of an iron-nickel alloy (69-31 per cent.), it was observed that about 25 per cent. of the austenite transformed, during sub-atmospheric cooling, within the time-interval of an audible click. This temperature point, designated M_b, occurs at or below M_s. The shock wave sent out from the specimen, freely suspended on a thread in the refrigerating liquid, was, in some cases, sufficiently intense to shatter the Dewar container, and to separate the toluene column in the immersed thermometer. The experiments reported in the present paper were carried out to determine the kinetics and the mechanism of this 'burst'.

The compositions of the alloys used are shown in the Table below: single-crystal specimens were prepared from alloy A, polycrystalline specimens from alloys B and C.

The experimental investigations made, recorded in considerable detail in the text, led to the following conclusions:—

'The reaction occurring during the burst is autocatalytic, i.e., the first transformation appearing in the burst provides the impetus for the nucleation of succeeding plates and so on.

'Martensite forms in amounts up to ½ per cent. above M_b (M_b is lower than, or equal to, M_s), and new plates are nucleated preferentially at the rims of previously formed plates on decreasing the temperature.

'Plastic deformation (slip) takes place locally at the martensite-austenite interface in plates formed above M_b, while substantial amounts of widely dispersed slip occur in the austenite during the burst.

'The thickness of plates formed above M_b is very much less than that of plates formed during the burst.

'Constraint to change-of-shape, as offered by Bakelite, depresses M_b but not M_s, and a decrease in the size of the specimen being constrained enhances the depression of M_b.

'Decrease in grain size depresses M_b, but does not measurably affect M_s.

'Prior plastic deformation in single crystals raises M_s and M_b, and reduces markedly the range of scatter of M_b values. Prior plastic deformation in polycrystals raises M_s, first raises then lowers M_b, and decreases total amount of transformation measured below the M_b for zero deformation.

'Further experiments, made to check the validity of the nucleation-and-growth theory, as applied to the burst phenomenon, showed that:—

'(1) Once formed, the martensitic plates do not thicken with decreasing temperature, as required by this theory.

'(2) The martensite range curve below M_b is insensitive to the austenitizing temperature for the iron-nickel alloys, which demonstrates the independence of the transformation upon distributions of athermal martensite embryos.

'(3) The grain-size explanation based on nucleation and growth is invalid for two reasons: (*a*) plates can exist which are not bounded at the ends by existing plates, grain boundaries or other such obstructions: (*b*) a direct dependence of plate thickness on length is predicted by the theory, and is not found when the grain size is decreased.

'(4) The concept of loss of coherency due to plastic

Alloy	Ni %	C %	N %	Mn %	Si %	P %	S %	Cr %
A	31±0·3	0·048	0·027	0·003	0·56	0·007	0·002	—
B	29·5±0·2	0·036	0·02	0·19	0·09	0·008	0·006	—
C	19·99	0·52	—	0·37	0·47	0·010	0·015	0·04

flow in limiting the size of plates, as proposed by Kurdjumow, has been found to be consistent with experiment.'

It is concluded that regions of internal strain are preferential sites for nucleation of martensite in these alloys. Two such regions are the internal strains within the virgin austenite and the internal strains at existing martensite plates. It appears that the nucleation is more sensitive to the state of strain than to variations in composition.

The authors advance a tentative explanation for the burst phenomenon, making use of the co-operative nature of the reaction in these alloys to nucleate new plates and thus generate a chain of transformation.

They consider that there is a possibility that many martensitic transformations involve bursts, of greater or lesser magnitude, and that, if this assumption proves to be correct, the burst phenomenon may provide a new basis for explanation of certain important features of martensitic transformation.

Influence of Alloy Additions on Transformations in Nickel-Iron Alloys

P. CHEVENARD and E. JOSSO: 'Influence of Additions on the Equilibrium Diagram of the Order ⇄ Disorder Transformation in Reversible Ferro-Nickel Alloys.' *Comptes Rendus*, 1951, vol. 233, Aug. 20, pp. 539-41.

An earlier communication (*ibid.*, 1950, vol. 230, p. 1467) showed that the critical temperature of the order ⇄ disorder transformation in binary nickel-iron alloys in the region of Ni_3Fe varies according to the nickel content, and corresponds to an equilibrium diagram with which it was correlated over the range 68 to 80 per cent. nickel. The present note relates to modifications effected by the presence of 5 per cent. of copper or 4 per cent. of molybdenum, over the range 64-76 per cent. nickel for the copper series and 70-78 per cent. nickel for the molybdenum-containing group.

Both addition elements lower the critical temperature of the transformation, and the presence of copper has the effect of shifting the maximum of the temperature/nickel-content curve which corresponds to the alloy most susceptible of ordering. It would therefore appear that the copper atoms have, in the superstructure, an influence somewhat similar to that of nickel atoms. Molybdenum, on the other hand, exerts merely a diluent effect, resulting in considerable lessening of the volume anomaly.

Young's Modulus of Iron-Nickel-Molybdenum Alloys

M. E. FINE and W. C. ELLIS: 'Thermal Variation of Young's Modulus in Some Fe-Ni-Mo Alloys.' *Jnl. of Metals*, 1951, vol. 3, Sept. (*Trans. Amer. Inst. Mining and Metallurgical Engineers*), pp. 761-4: T.P. 3131E.

In certain binary iron-nickel alloys which have been cold-worked and subsequently stabilized by stress-relief annealing, Young's modulus values are found to be almost invariant over a substantial temperature range, the exact limits of which are determined by composition and treatment: (see *Trans. Amer. Inst. Min. Met. Eng.*, 1950, vol. 188, pp. 1120-5; *Nickel Bulletin*, 1950, vol. 23, No. 11, p. 208). The present report records determination of the effect of molybdenum additions to such alloys.

Four series of alloys were used, having, respectively, molybdenum contents of 5, 7, 9 and 10 per cent., and containing 47 to 58 per cent. of iron. Young's modulus was determined on all the alloys at a series of temperatures over the range $-50°$ to $+100°C.$, by the dynamic method used in the earlier experiments, *loc. cit.*

A detailed study of the effect of cold working was made on two of the alloys: 5·3/41·7 and 10·7/40·1 molybdenum-nickel, respectively, and the influence of change in annealing temperature was examined on an alloy containing 9·9 per cent. molybdenum with 42·8 per cent. nickel.

The results show that in the ternary alloys, as in the binary iron-nickel series, the temperature interval of almost constant Young's modulus is greatly extended by work-hardening. A stress-relief annealing treatment is necessary, in order to stabilize the alloys.

Sensitivity of the thermal coefficient to variation as a function of nickel content is decreased, by approximately a factor of two, by addition of 9-10 per cent. of molybdenum. In alloys of such composition the mean thermal coefficient of modulus for the temperature range $-50°$ to $+100°C.$ varies from $+50$ to $-50 \times 10^{-6}/°C.^{-1}$ as the nickel varies from 36·5 to 41·5 per cent.

An alloy containing molybdenum 9, nickel 38-41·5 per cent., balance iron, has, in the cold-worked condition, a low temperature coefficient of Young's modulus, substantial magnetic permeability (which is reasonably constant over a limited range of temperature), and high mechanical strength. The coefficient of modulus can be controlled by regulation of the iron:nickel ratio, and a further measure of control can be exercized by modification of the straining-annealing treatment.

The authors explain the principal effects of molybdenum, on the temperature dependence of modulus, by assuming that molybdenum decreases the modification in the interatomic energy-interatomic distance relation from the energy of magnetization.

Nickel-Iron Alloys of Controlled Expansion

MOND NICKEL CO., LTD.: 'The Nilo Series of Controlled Expansion Alloys.' *Publn.* 500*, 1951: 8pp.

The Nilo alloys have been developed for use in applications in which controlled low and intermediate coefficients of thermal expansion are required, e.g., in machine parts where change of dimensions with variation in temperature is undesirable, in thermostats, and in glass-to-metal seals.

The type compositions of the respective alloys in the series are shown in the Table on p. 237.

The individual characteristics of the respective alloys are detailed in this publication and their specific applications are discussed. Curves show the coefficient of expansion and total expansion over various temperature ranges, in comparison with the properties of

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	Nickel %	Cobalt %	Chromium %	Iron %
Nilo 36 ..	36	—	—	Bal.
Nilo 40 ..	40	—	—	
Nilo 42 ..	42	—	—	
Nilo 48 ..	48	—	—	
Nilo 50 ..	50	—	—	
Nilo K ..	29	17	—	
Nilo 475 ..	47	—	5	

65-35 brass, and tables give average physical properties, and mean linear coefficients of expansion of annealed materials, and their inflexion points.

CAST IRON

Spheroidal-Graphite Cast Iron: Properties and Uses

MOND NICKEL CO., LTD.: 'Spheroidal-Graphite Cast Iron: Some Properties and Applications.' *Publn.* 455*, 1951: 18 pp.

Based on a paper presented by A. B. EVEREST to Inst. Brit. Foundrymen, June, 1950: see abstract in *Nickel Bulletin*, 1950, vol. 23, No. 7, p. 130.

The material in the original paper has been supplemented by additional illustrations of applications of the new irons, and by photomicrographs showing structures typical of flake-graphite and spheroidal-graphite cast irons.

Determination of Cobalt in Nickel-containing Materials

See abstract on p. 234.

CONSTRUCTIONAL STEELS

Effects of Retained Austenite in Nickel Steel

E. F. BAILEY and W. J. HARRIS: 'Effects of Decomposition of Retained Austenite during Tempering on Notch Toughness and Tensile Properties .' *Amer. Soc. Metals, Preprint* 19, Oct., 1951; 14 pp.

The effects of retained austenite present in quenched low-alloy medium-carbon steels depend on whether it remains as austenite during the test, whether it transforms during testing, or whether it was decomposed during tempering prior to test. The present authors reported in an earlier paper that retained austenite, *per se*, had little effect on impact and tensile properties, but that if martensite was formed from the retained austenite, either by plastic deformation or by low-temperature treatment, notch-toughness and tensile ductility were reduced and tensile strength was raised.

In most low-alloy, medium-carbon steels the austenite is decomposed during normal tempering operations, and the kinetics of the decomposition of retained austenite have been shown to be similar to those of decomposition of primary austenite.

The investigation reported in the present paper was undertaken to determine the influence of the amount and type of decomposition product, on impact and tensile properties. For comparison, properties of the products of primary austenite decomposition were examined, and oil-quenched and tempered structures were also examined. The steel on which the work was done was of the following composition: carbon 0·40, manganese 0·89, silicon 0·35, phosphorus 0·006, sulphur 0·017, nickel 3·34, chromium 0·10, per cent.

Specimens of this steel were quenched below M_S, to give 10, 40, 70 and 90 per cent. retained austenite, and a metallographic study was made of the decomposition of this austenite during tempering at 600°, 800°, 900° and 1050°F. (316°, 426°, 482° and 565°C.).

It was found that, in this steel, decomposition of retained austenite reduces notch toughness only when pearlite is formed. Pearlite may be formed by decomposition of retained austenite when 70 per cent. or more of austenite is present, and when tempering is carried out at 900°F. (482°C.) or above. With 40 per cent. or less of retained austenite, aggregates of acicular ferrite-plus-carbides are the final microstructure after tempering, even when the treatment is done in the range of temperature in which pearlite would form during primary decomposition.

Acicular bainite formed from primary austenite showed better mechanical properties than non-acicular bainite resulting from primary austenite. Martensite formed below 300°F. (150°C.) appears to have lowered toughness, particularly when tempered to hardnesses above Rockwell C-40.

Influence of Nickel on Transition Temperature in Pearlitic Steels

J. A. RINEBOLT and W. J. HARRIS: 'Effect of Alloying Elements on Notch Toughness of Pearlitic Steels.' *Trans. Amer. Soc. Metals*, 1951, vol. 43, pp. 1175-1201; disc., pp. 1201-14.

Report of work carried out to establish the quantitative effects of alloying elements on tensile properties and notch toughness of pearlitic steels. Variables other than composition were held as constant as possible.

The basis composition was carbon 0·30, manganese 1·00 and silicon 0·30, per cent.: the following elements were progressively varied, up to the amounts shown in brackets: aluminium (0·092), boron (0·0044), carbon (0·67), chromium (0·95), copper (2·00), manganese (1·55), molybdenum (0·29), nickel (3·15), phosphorus (0·21), sulphur (0·137), silicon (3·05), titanium (0·39), vanadium (0·21). Additivity effects and influence of variations in ratio carbon/manganese, carbon/nickel and manganese/nickel were also studied.

Impact tests were made at temperatures between −315° and +600°F. (−193° and +315°C.), and duplicate tensile tests were carried out at room temperature on all the steels. The results of the impact tests are assessed on the basis of four of the most generally

*Copies of this publication will shortly be available.

used definitions of transition temperature. The average energy transition temperature of Charpy V-notch specimens broken over a range of temperature was finally selected for evaluating the effect of the alloy elements.

All the steels were cooled at a rate of 25°F. (14°C.) per minute from the austenitizing temperature, a treatment which produced a coarse pearlitic structure of equivalent pearlite spacing for all the materials investigated.

The following tabulation shows the effect, on transition temperature, of increase in the respective addition elements:—

Table I

Increase Transition Temperature	Decrease Transition Temperature	Raise and then Lower Transition Temperature	Lower Transition Temperature and then No Change
Boron Carbon Chromium Copper Molybdenum Phosphorus Silicon	Manganese Nickel	Titanium Vanadium	Aluminium

Effects of carbon, manganese and nickel appeared to be almost additive.

The only tensile property which showed even fair correlation with transition temperature was reduction of area. Good correlation was established between maximum energy and reduction in area.

It was observed that alloying elements affect the entire-energy vs. temperature curve in different ways. It is therefore considered that a study of a single transition temperature may leave out of account many important effects.

Discussion on this paper included a contribution from H. W. G. HIGNETT, reporting data demonstrating that nickel depresses the transition temperatures of normalized steels containing large amounts of free ferrite, and also those of hardened-and-tempered steels in which the carbide is uniformly dispersed. The steels on which the tests were made contained carbon 0·15–0·16 per cent., with nickel 2·01, 3·04 and 4·70, per cent.

See also related paper abstracted below.

J. A. RINEBOLT and W. J. HARRIS: 'Comparison of the Effects of Alloying Elements on the Lower and Upper Transition Temperatures in Pearlitic Steels.' *Amer. Soc. Metals, Preprint* 20, Oct., 1951; 12 pp.

The paper opens with a succinct review of earlier literature on transition temperature and its correlation with service performance. Relatively close correlation has been found to exist between service failure and the temperature at which the 6–12 ft.-lb. level occurs on the Charpy V-notch test transition curve: it has therefore been suggested that the 15 ft.- lb. transition temperature should be used to establish minimum safe operating temperature.

STOUT and McGEADY (*Welding Jnl.*, 1948, vol. 27, Suppl. pp. 299-302) have suggested that the curve includes two energy transitions, one associated with a change in the appearance of the fracture, and the other, at a lower temperature, with the disappearance of the last traces of ductility. The work reported in the present paper was undertaken to establish the effects of composition of the steel on the lower transition, and to correlate the effects of various alloying elements, on that point, with their influence on the upper point (already studied by the same authors: *see preceding abstract*).

A summary of the quantitative effects of composition on the lower transition is shown in Table II below, in comparison with their effects on average energy value and the 15 ft.-lb. transition temperatures, as determined in the earlier investigation.

The comparison shows that manganese and phosphorus are the only elements which have approximately the same effect on all transitions. With carbon, nickel, and silicon (0·10 - 1·03 per cent.) the effect on the lower transition is different from that exerted on the upper one. For carbon below 0·30 per cent. and silicon above 1·03 per cent. there is good agreement for the shifts in the lower and the 15 ft.-lb. transition temperatures. For the other ranges of carbon and silicon, and for the full range of nickel additions, the 15 ft.-lb. transition is a poor approximation of the lower transition.

Table II
Effect of Alloying Elements on Shifts of Transition Temperatures

Alloy Added	Limit of Addition Studied (%)	Shift of Transition Temperatures		
		Lower Transition (°F. per 0·01%)	15 ft.-lb. (°F. per 0·01%)	Upper Transition Average Energy (°F. per 0·01%)
C	0·57	1·6	(2·4–5)*	6
Mn	1·55	−1·0	−1·0	−1·0
Ni	3·15	−0·5	−0·3	−0·1
N	0·019	0	0	0
P	0·20	10	11	13
Si	0·1 to 1·0	−0·70	0†	0‡
	1·0 to 2·67	1·3	1·2	1·2
Ti	0·40	0	0	0

* The 2·4 value applies up to 0·30 per cent. carbon; the 5 above.
† The 0 applies up to 0·6 per cent. silicon; the 1·2 above 0·6.
‡ The 0 applies up to 0·2 per cent. silicon; the 1·2 above 1·2

Properties of Segregates in Nickel-Alloy Steel Forgings

H. M. FINNISTON and T. D. FEARNEHOUGH: 'Physical and Mechanical Properties of Segregates in Two Alloy Steels.' *Jnl. Iron and Steel Inst.*, 1951, vol. 169, Sept., pp. 5-12.

In connexion with the use of large alloy-steel forgings for important naval armaments, the Bragg Laboratory (Naval Ordnance Inspection Department), Sheffield, has made an extensive investigation of the metallurgical nature and characteristics of the segregates in such forgings. The early part of the research was devoted to development and application of a spectrographic technique for micro-analysis of individual segregates (see reports in *Jnl. Iron and Steel Inst.*, 1941, vol. 144, pp. 183P–201P and 1945, vol. 152, pp. 473P–507P). In late 1943 the work was extended to cover study of the physical and mechanical properties of the segregates, and it is with this aspect that the present paper is concerned.

The work was done on forgings of two types of steel of the following compositions:—

C %	Si %	Mn %	P %	S %	Ni %	Cr %	Mo %	V %
0·37	0·24	0·70	0·035	0·034	3·61	0·17	0·10	—
0·41	0·19	0·74	0·021	0·031	2·46	0·13	0·10	0·11

Both steels were made in the acid open-hearth furnace, and were top-poured in wide-end-up moulds. The nickel-steel ingot weighed 20 tons and the nickel-vanadium steel ingot 37 tons. After a forging reduction of approximately 2:1 in both cases, a full transverse section from the top discard from each forging was obtained for examination of the segregates. Sulphur prints were taken, and segregates isolated from the steels were examined by hardness, tensile and notched-impact testing, by determination of composition (spectrographic and micro-chemical tests), and by observation of macro- and micro-structure. Technique used in each type of test is described. Quantitative differences in properties, between the segregates and the matrices surrounding them, were examined after various heat-treatments.

The following conclusions are drawn from the observations made:—

There is a hardness gradient across each segregate, at a higher level than that of the matrix surrounding the segregate. A difference in hardness between segregate and matrix persists in all hardened and tempered samples, whatever the hardness level. The greater hardness of the segregates, by comparison with their adjacent matrices, is reflected in their higher proof and maximum stresses. Their elongation and notched-impact values are generally lower, in some cases markedly so.

There is a composition gradient across the segregates, rendering them more highly alloyed in nickel, vanadium, and molybdenum than the adjacent matrix. There is also a general increase in carbon, sulphur, and phosphorus content (particularly the latter), but the precise gradient of composition of the metalloids has not yet been established.

Macrostructural differences across the width of segregates were observed: these are believed to be due to variations in composition. Segregates were found, however, to contain more non-metallic inclusions than the adjacent matrix, and it is considered that the incidence of these inclusions at the stressed surface of test specimens probably accounts for some of the very low values of maximum stress, impact value, and elongation reported. It is thought that there is probably some physical similarity between the non-metallic inclusions and Griffith's cracks in other materials.

Segregates appear to be the concentrated metal, and, when liquid, are entrapped between the main spines of solidifying dendrites, which surround them. Metal in the interdendritic arms shows variations in hardness and composition comparable with those shown by segregates.

X-Ray Studies on Temper-Brittle Steels

S. R. MALOOF: 'Some X-Ray Diffraction and Electron-Microscope Observations on Temper-Brittle Steels.' *Amer. Soc. Metals, Preprint* 22, Oct., 1951; 11 pp.

The work described was concerned primarily with the examination of the lattice structure of four alloy steels showing varying degrees of susceptibility to temper-embrittlement. The compositions of the steels used are shown in the Table below.

All the steels were austenitized at 1560°F. (850°C.), in an electric furnace; the samples were placed in a carbon block during heating, to prevent excessive decarburization. After one hour at temperature, they were oil-quenched to room temperature. Tempering was carried out in a small lead pot, the embrittling

S.A.E. Type	C %	Mn %	Si %	S %	P %	Ni %	Cr %	Mo %
3140 } Commercial	0·41	0·79	0·29	0·018	0·014	1·21	0·80	Trace
4340 } Commercial	0·44	0·73	0·26	0·024	0·025	1·86	0·86	0·23
3312 } Commercial	0·09	0·50	0·27	0·014	0·014	3·45	1·55	0·06
Vacuum-melted ..	0·15	0·40	0·01	0·014	0·004	3·60	1·38	Trace

treatment consisting of tempering for one hour at 1200°F. (650°C.), followed by slow cooling (34°F.: 19°C. per min.) to 600°F. (316°C.) and water-quenching to room temperature. The non-embrittling treatment comprised water-quenching to room temperature after soaking for one hour at 1200°F. (650°C.).

The results show that, in all four steels, the embrittling treatment given causes definite decrease in lattice parameter of ferrite. The authors are of the opinion that this decrease is probably due more to the precipitation of carbide from supersaturated ferrite than to the change of alloy concentration in cementite. The extreme fineness of some of the carbide particles observed in the electron micrographs of the embrittled samples of the 3312 steel is offered as a possible explanation of the greater susceptibility to temper-embrittlement of these steels, in comparison with the 3140 and 4340 types.

It is suggested that if this conception of carbide size and uniformity (probably controlled to a marked degree by the extent of the alloy enrichment) is an exact explanation of temper-brittleness, it should be possible for a steel to regain its toughness after being heated for a prolonged period at the embrittling temperature. Data on a temper-brittle 1 per cent. chromium steel, in which toughness was restored by such prolongation of treatment, are recorded, and the explanation is advanced that the steel regains its toughness, with decrease in hardness, by agglomeration and growth of the precipitated particles beyond a critical size which is such as to embrittle the steel. The constancy observed in the lattice parameter is believed to be a fair indication that the composition of the ferrite does not change during this process.

Low-Temperature Fractures in Tempered Nickel-Alloy Steel

A. R. ENTWISTLE: 'Low-Temperature Fractures in Tempered Alloy Steels.' *Jnl. Iron and Steel Inst.*, 1951, vol. 169, Sept., pp. 36-8. (*British Iron and Steel Research Association Paper MG/A/91/51.*)

As part of an investigation of temper-brittleness, a study has been made of fractures in plain-carbon and low-alloy steels at low temperatures: the latter steels were examined in various states of temper-embrittlement. In 1948, McLEAN and NORTHCOTT reported examination of low-temperature fractures in tempered steels in the tough and the brittle conditions, and observed a leaf-like structure characteristic of the steels in the tough condition. The present paper reports a more detailed examination of fractures obtained under experimental conditions producing brittle fracture. The steel used was En 23, having the following composition: carbon 0·41, silicon 0·70, manganese 0·43, sulphur 0·0295, phosphorus 0·024, arsenic 0·085, chromium 0·66, nickel 3·01, molybdenum 0·05, per cent.

The results show the cleavage type of failure to be related to the original martensite structure developed on quenching: under certain conditions both cleavage and intergranular failure may occur in the same fracture. Plain-carbon steels similarly heat-treated show cleavage, but not intergranular, fracture.

Surface Hardening of Steel

G. T. COLEGATE: 'The Surface Hardening of Steel. Part VIII Nitriding' (contd.). *Metal Treatment and Drop Forging*, 1951, vol. 18, Sept., pp. 419–25.

This instalment amplifies the discussion of nitriding begun in the August issue. It opens with a consideration of the *dissociation of ammonia*, by which nitriding is effected, and of methods which have been proposed for securing correct dissociation and efficient nitriding action. The effect of degree of dissociation, on the depth of case-hardening produced in a nitrided steel, is graphically shown.

Although nitriding furnaces are usually of the batch type, it is pointed out that the semi-continuous form has considerable advantages for such treatment: a typical modern unit is illustrated.

With regard to methods adopted for *selective nitriding*, the author discusses the advantages and limitations of (*a*) metallic coatings (copper, nickel, lead-tin solder, or tin), and (*b*) paste-type coatings, which may, or may not, contain a metallic constituent. Class (*a*) are to be preferred, as giving more consistent and reliable protection: class (*b*) materials are cheaper, and have advantages for application to some areas which could not so easily be sealed off by deposition of metal coatings.

The *temperature optimum for nitriding* is more critical than that used in the various carburizing processes: normally the range is about 460°–530°C. for ordinary nitriding steels, though temperatures outside these limits have been successfully employed in commercial operation. For each particular class of nitriding steel there is an even more closely restricted range of temperature: treatments are considered by the author in relation to typical steels, and the influence of temperature, as affecting depth and character of case, is reviewed.

The *length of time required for nitriding* is a disadvantageous feature of the process, and attempts have been made to accelerate the reaction by the use of various types of catalyst, e.g., aluminium, copper, turnings of nitrided steels, and non-metallic powders, such as magnesia. These substances appear to assist formation of molecular hydrogen from atomic hydrogen and thereby reduce the denitriding effect of this gas.

Finally, some consideration is given to *warpage and growth*, as factors which must be taken into account in treatment of parts requiring accurate finished dimensions. Means for minimizing these effects are briefly discussed.

For *softening* of nitrided steels a molten mixture of sodium and potassium chlorides is used.

Nickel-containing Die and Tool Steels

H. J. MERCHANT: 'Die and Tool Steels for the Drop Forging Industry.' *Metal Treatment and Drop Forging*, 1951, vol. 18, Aug. and Sept., pp. 369-76, 379; 401-6.

Earlier articles by the same author (*ibid.*, 1949, vol. 16, pp. 3-11, and 1951, vol. 18, pp. 13–21, 24) emphasized the importance of the quality of the steel used for dies and tools; they dealt exclusively with

die blocks used in regular impact forging, as carried out in belt-type, board, air-lift or double-acting steam hammers.

The present article discusses compositions, properties and uses of die and tool steels for horizontal upsetter and vertical-press forging practice, including roll-forging dies, hammer-die inserts, and steels used for ancillary operations of trimming and punching. The applications of nickel-chromium-molybdenum and silicon-nickel-chromium-molybdenum steels are among those considered.

Determination of Hydrogen in Nickel-Alloy Steels

R. M. COOK and J. D. HOBSON: 'Determination of Hydrogen in Liquid Steel.' *Jnl. Iron and Steel Inst.*, 1951, vol. 169, Sept., pp. 23-4. (*British Iron and Steel Research Association Paper SM/BB/102/50.*)

The modified notched-pencil test for determination of hydrogen in liquid steel, described by WELLS and BARRACLOUGH (*ibid.*, 1947, vol. 155, pp. 27-32) has been used by the Brown-Firth Research Laboratories for several years, to control hydrogen content during manufacture of low- and high-alloy steels by the electric-arc and the acid open-hearth processes. The sealed-mould test, described by SPEIGHT and COOK (*ibid.*, 1948, vol. 160, pp. 397-406) was developed by The United Steel Companies, Ltd., and has proved suitable for determining possible hydrogen variations in steels made by the basic open-hearth and electric-arc processes.

Since data obtained by the two methods, on similar steels, had appeared to give slightly different results, a direct comparison has been made on identical samples of a range of low-alloy steels containing nickel, chromium and molybdenum, singly or in various combinations, made by the three processes—acid and basic open-hearth, and basic electric-arc. The technique of both methods of estimation is briefly described, and the results of the determinations are recorded in the present paper.

The satisfactory agreement shown between the results obtained by the two methods indicates that both are satisfactory if carefully carried out, by experienced operators. For control purposes, the notched-pencil procedure has the advantage of being the more rapid.

HEAT- AND CORROSION-RESISTING ALLOYS

British Specifications for High-Nickel Alloys

HENRY WIGGIN AND CO., LTD.: 'Some Official Specifications for Wiggin High-Nickel Alloys.' *Publn.* 544*, 1951; 2 pp.

Tabular summary of B.S. and D.T.D. specifications covering various forms of the following materials:—Nimonic 75, Nimonic F, Nimonic 80, Nimonic 80A, Nimonic 90; Inconel; Monel; K Monel; Nickel; Electrical-Resistance Materials.

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Sigma Formation in Nickel-Chromium Steels

M. E. NICHOLSON, C. H. SAMANS and F. J. SHORTSLEEVE: 'Composition Limits of Sigma Formation in Nickel-Chromium Steels at 1200°F. (650°C.).' *Amer. Soc. Metals, Preprint* 13, Oct., 1951; 19 pp.

The accuracy of constitutional diagrams of the nickel-chromium-iron system, as determined by various investigators, is critically considered as an introduction to the present work. It is believed that the diagram generally accepted as being most satisfactory for alloys of commercial purity is that established in 1939 by SCHAFMEISTER and ERGANG (*Archiv f.d. Eisenhüttenwesen*, 1939, vol. 12, p. 459). Since, however, it has subsequently been shown that sigma may form at 650°C. in chromium steels containing as little as 21 per cent. chromium (whereas the diagram of Schafmeister and Ergang indicates that the minimum chromium content of the sigma regions for iron-chromium alloys is 33 per cent. at that temperature), it was considered possible that the iron-chromium-nickel portion of their diagram might also be in error, and that the regions of sigma stability extend to lower values of chromium than they have indicated. If such a presumption could be proved, it would mean that some important heat-resisting steels which had previously been believed to lie outside the regions of sigma formation might be susceptible to embrittlement from that cause.

In view of the above considerations, the authors undertook a re-determination of the limits of the sigma regions at 650°C., in chromium-nickel steels, of simulated commercial purity, containing up to 21 per cent. chromium and up to 20 per cent. nickel. The five series of steels actually studied contained, nominally, 2, 4, 8, 14 and 20 per cent. nickel, with chromium ranging from 12 to 21 per cent. Silicon, manganese, phosphorus, sulphur and carbon were present in normal steelmaking percentages, but in no case did the carbon exceed 0·1 per cent. One industrial steel, Type 304, was also included. The steels containing 2, 4 and 20 per cent. nickel were in the cast condition, the 8 and 14 per cent. nickel grades in the hot-rolled state.

In order to promote uniformity, the steels were soaked for 64 hours at 2250°F. (1230°C.) and water-quenched. Powder samples of each material were then sealed in Vycor tubes, under partial vacuum, and were held at 1200°±10°F. (650°±5°C.), for 500, 1,000 or 2,000 hours, followed by air cooling.

In the second section of the investigation the influence of silicon (0·5–3 per cent.), manganese (0·5–2 per cent.) and molybdenum (up to 2 per cent.), on the sigma-forming limits of composition, were determined.

The conclusions drawn from both sections of the research are summarized below:—

Under conditions approximating equilibrium, sigma phase will form in chromium-nickel stainless steels containing approximately 5 per cent. less chromium than is indicated by the previously accepted constitutional diagram of Schafmeister and Ergang.

This new delineation of the sigma-forming boundaries places at least portions of the composition ranges

of the important types of commercial austenitic steels within the sigma-forming range, and explains some of the apparently anomalous observations reported on the occurrence of sigma in such steels.

In the vicinity of the gamma triple point, which lies close to 8 per cent. of nickel, sigma will not form in steels having a chromium content of less than 17·7–18·1 per cent.

The authors consider that, for elevated-temperature applications, Type 302 steel appears to be the grade of 18-8 which will show least susceptibility to sigma formation. For complete freedom from sigma in low-carbon (0·12 per cent. or less) steels of this type, a composition range of 16 to 18 per cent. chromium and 8 to 10 per cent. nickel is indicated.

The sigma-forming composition limits for stainless steels of simulated commercial purity are almost identical with those for high-purity alloys in the gamma region, but deviate increasingly toward lower chromium contents as the nickel content of the alloys decreases. At about 2 per cent. nickel the alpha triple point of the high-purity diagram has a chromium content about 8 per cent. higher than the corresponding point on the steel diagram.

For all nickel contents below about 20 per cent., silicon displaces the $(\gamma+\sigma)/\gamma$ boundary towards lower chromium contents. The first 1 per cent. of silicon displaces this phase boundary only about 0·5 per cent. chromium at the 20 per cent. nickel level, but the boundary appears to be displaced further by about 1·5 per cent. chromium for each additional per cent. of silicon, up to at least 3 per cent. The effect of manganese cannot be stated with certainty, but it is concluded that amounts of manganese up to about 2 per cent. have little or no effect on the sigma-forming tendencies of steels containing up to 2 per cent. of silicon.

For nickel contents below about 1·5 per cent., tendency to sigma formation is materially increased by addition of about 2 per cent. molybdenum: in nickel-free steels $(\alpha+\gamma)/\alpha$ line probably terminates in the region of 16-18 per cent. chromium.

Carbides in Nickel-containing High-Temperature Alloys

J. R. LANE and N. J. GRANT: 'Carbide Reactions in High-Temperature Alloys.' *Amer. Soc. Metals, Preprint* 10, Oct., 1951, 22 pp.

A large number of the alloys now used for high-temperature applications contain substantial percentages of cobalt. The carbon content of such alloys is always in excess of the solubility limit, and primary and eutectic carbides therefore occur on solidification. In addition, re-heating of the cast alloys causes formation of an ageing precipitate, which is a carbide. All these compounds have an important influence on the mechanical properties of the materials.

In this paper the authors report a study of the identification of the carbides present in cast and heat-treated alloys, and discuss the transformations involved. The materials considered were of the following types:—

(1) A group of Vitallium-type alloys, containing cobalt 70, chromium 24, molybdenum 6, per cent., with a wide range of carbon content.
(2) N-155, a complex cobalt-chromium-nickel-iron alloy containing niobium and other carbide-forming elements.
(3) S-816, a complex cobalt-chromium-nickel alloy containing niobium and other carbide-forming elements.
(4) 70 J, a high-carbon Vitallium-type alloy modified by additions of nickel and tantalum.

Full details of composition of all the alloys are given in the paper.

The procedure used involved microscopic examination of the alloys (including quantitative measurement of the phases), and also separation of the carbides by an electrolytic process. The separated carbides were analyzed chemically and by X-ray diffraction.

It was found that in the cast condition most of the alloys contained either Cr_4C or Cr_7C_3, depending on the carbon content: these were present in association with a smaller amount of the double carbide M_6C. In alloys containing tantalum or niobium the corresponding carbides were found.

The authors were unable to find any etchant which would distinguish clearly between Cr_4C and Cr_7C_3, but the M_6C carbides could be preferentially darkened by heat-tinting or by electrolytic etching in an alkaline solution.

Ageing at 1350°–1600°F. (730°–870°C.) caused formation of a precipitate of Cr_4C, and also converted Cr_7C_3 to Cr_4C.

Difference in cooling rates through the freezing range, caused by variation in section, did not appreciably affect the variety of the carbides which formed, except that a somewhat larger amount of M_6C formed in the rapidly cooled than in the slowly cooled sections.

The simpler cobalt-base alloys, of the Vitallium type, were mostly hexagonal as cast, but during ageing they transformed to face-centred cubic. The more complex alloys were cubic under all conditions.

Attention is directed to the importance of nitrogen as an alloying element. Its effect is similar to that of increase in carbon content, and was especially clearly marked in the N-155 alloy.

Influence of Cold Work on Creep-Resistance

D. N. FREY and J. W. FREEMAN: 'Fundamental Effects of Cold Working on the Creep Resistance of an Austenitic Alloy.' *Jnl. of Metals*, 1951, vol. 3, Sept. (*Trans. Amer. Inst. Mining and Metallurgical Engineers*), pp. 755-60: T.P. 3129E.

The research reported was carried out with the dual aim of ascertaining the fundamental reasons underlying the improvement observed in creep-resistance of austenitic alloys resulting from cold work, and of evaluating accurately the conditions in which cold working may be expected to improve creep-resistance.

To this end, resistance to creep and internal structure were correlated for a variety of cold-worked conditions, using, as a typical alloy, low-carbon N-155 Multimet, in the form of $\frac{7}{8}$-in. square bar stock. The composition of the alloy used is given as carbon 0·13, manganese 1·43, silicon 0·34, chromium 20·73, nickel 18·92, cobalt 19·65, molybdenum 3·05,

tungsten 1·98, niobium 0·98, nitrogen 0·14, per cent., iron balance.

The work was done in two parts:—

(1) the influence of cold working, on creep rate under a single stress at 1200°F. (648°C.), was determined. The specimens used had been reduced approximately 5, 15 and 40 per cent. at room temperature, and 15 per cent. at temperatures up to 2200°F. (1204°C.).

(2) the influence of annealing at 1200°, 1400°, 1600° and 1800°F (648°, 760°, 871° and 981°C.), for periods up to 1000 hours, was studied. In this series of experiments attention was concentrated on materials which had been rolled approximately 5, 15 and 40 per cent. at room temperature and 15 per cent. at 1400°F. (760°C.).

The creep tests were carried out at 1200°F. (648°C.) under 40,000 p.s.i. (18 tons per sq. in.), this value being approximately the 1,000-hour rupture stress of the low-carbon N-155 alloy as reduced 15 per cent. No transient creep was observed, and all tests were run for periods of 200 to 500 hours, i.e., sufficiently long to establish the steady-state rate of creep. Structural effects of cold working were studied primarily by X-ray diffraction, but microscopic examination, both optical and electronic, was also used.

The observations recorded lead to the conclusion that cold working improves the creep-resistance of low-carbon N-155, and probably other alloys of the same general type, through the presence of elastic stresses left in the lattice after the working operations.

For any given reduction, optimum improvement in creep-resistance may be obtained with any temperature of reduction below that which will allow relaxation of the internal stresses to a marked degree during the actual working operation. For reductions of 15 per cent., on the alloy studied, this useful working temperature-range is from 80° to 1500°F. (27° to 815°C.).

Conversely, increasing amounts of cold working confer increasing resistance to creep only up to the point at which the internal stresses are so high as to permit relaxation to occur in significant amount at the particular service temperature under consideration. It is also concluded that the critical amount of cold reduction decreases as the service temperature is raised. For low-carbon N-155, for service use or test at 1200°F. (648°C.), the critical degree of cold reduction is approximately 25 per cent.

Correlation was found to exist between the logarithm of creep rate against internal stress, as measured by width of diffraction lines. This relation existed for solution-treated and cold-rolled low-carbon N-155, whether the material had undergone subsequent annealing treatment or had not been so treated. The full quantitative significance of this correlation cannot be fully assessed until a more exact interpretation of the broadened diffraction lines can be achieved, but it is noted that the relationship agrees qualitatively with predictions made from the Eyring reaction-rate theory of creep.

Relation between Static and Fatigue Properties of High-Temperature Alloys

'Co-operative Investigation of Relationship between Static and Fatigue Properties of Heat-Resistant Alloys at Elevated Temperature. *Nat. Advisory Committee for Aeronautics, Research Memorandum RM* 51A04, Mar. 7, 1951; 51 pp.

This is an interim report, issued under the sponsorship of a committee which is (1) studying relation of static and fatigue properties at high temperatures, and (2) attempting to build up data which will provide an improved basis for evaluating results of tests made on different types of fatigue-testing machine.

The report now published relates to tests on low-carbon N-155, of the following composition: carbon 0·13, manganese 1·64, silicon 0·42, chromium 21·22, nickel 19·00, cobalt 19·70, molybdenum 2·90, tungsten 2·61, niobium 0·84, nitrogen 0·13, per cent. The tests made embodied combinations of steady tensile stress with superimposed dynamic stress, as well as completely-reversed-stress fatigue tests. Determinations were made at room temperature and at 1000°, 1200°, 1350° and 1500°F. (538°, 648°, 734° and 815°C.). The results are summarized as curves of alternating stress against mean stress, for fracture in 50, 150 and 500 hours. Some creep data under combined-stress conditions, and a summary of the fracture characteristics of the specimens in the various tests, are also recorded.

High-Temperature Properties of 16-25-6: Effect of Duration of Test

C. L. CLARK, M. FLEISCHMANN and J. W. FREEMAN: 'Influence of Extended Time on Creep and Rupture Strength of 16-25-6 Alloy.'

Amer. Soc. Metals, Preprint 16, Oct., 1951; 20 pp.

The paper reports tests varying in time period up to 12,000 hours, at temperatures of 1200°, 1300° and 1400°F. (650°, 705° and 760°C.), on two heats of material (see Table below).

The material was tested in two different conditions:—

(1) 1-in. round bars were water-quenched from 2150°F. (1175°C.),a treatment considered most practical for solution of carbides, and also imparting minimum hardness.

(2) 1-in. round bars were reduced about 25 per cent. by finish-rolling at 1500°F. (815°C.), and were then

C %	Si %	Mn %	P %	S %	Ni %	Cr %	Mo %	N %
0·08	0·62	1·90	0·011	0·016	25·31	16·21	6·30	0·154
0·08	0·56	1·64	0·027	0·016	25·00	16·35	5·91	0·141

tempered for 6 hours at 1275°F. (690°C.). In this case the finish-rolling (hot-cold work) produced considerable cold work, while the subsequent tempering treatment relieved some of the cold-work stresses, and thus added to the stability of the material.

The respective hardnesses after the two treatments were 188 and 308/321 Brinell. Mechanical properties of the two heats at room temperature show that the hot-cold-work treatment had much increased the strength, without undue sacrifice of ductility.

The data on prolonged creep and stress-rupture tests, together with observations on the structural condition of the alloys, and examination of the room-temperature properties after high-temperature exposure, lead to the conclusion that time of test has a much greater effect on creep rate (and thus on reported creep strength) than on rupture strength. For example, at 1200°F. (650°C.) about 8,000 hours were required to obtain the minimum creep rate corresponding to a given stress, whereas tests of 2,000 hours' duration would have given approximately the same stress-rupture characteristics as were shown by the more prolonged tests.

In contrast to its effect on original room-temperature mechanical properties, the hot-cold-work treatment did not appreciably affect minimum creep rates at the temperatures used in these tests. The treatment did, however, reduce the total elongation during creep test, and improve rupture strength at 1200°F. (650°C.). At 1400°F. (760°C.) a reverse effect was observed.

Electron micrographs of the 16-25-6 alloy show that, at the temperatures under consideration, its strength is due to precipitation effects, a fact which explains (*a*) the decrease in total ductility-to-fracture observed with lengthening time of test, and (*b*) decrease in room-temperature ductility and impact resistance of specimens after creep test.

In many cases the 100,000-hour rupture strength was found to be less than the stress for a creep rate of 0·01 per cent. per 1,000 hours, a finding which throws doubt on the validity of the equivalence of 0·01 per cent. per 1,000 hours and 1·0 per cent. per 100,000 hours, which is often assumed by designers. This fact may also indicate that ductility-to-fracture will be less than that corresponding to a creep rate of 1 per cent. in 100,000 hours.

The 16-25-6 alloy enters the third stage of creep after relatively small amounts of deformation, but the duration of the third stage was found to be about equal to that of the first and second stages combined, i.e., entry into the third stage does not imply immediate failure.

Prolonged high-temperature tests, e.g., of 10,000 hours' duration, are highly desirable as a basis of design for components for which a life of several years is to be anticipated. Where such long-term tests are not possible, however, it is considered that stress-rupture characteristics (as obtained from periods of the order of 2,000 hours), rather than creep properties, form the more reliable criterion, particularly in the case of complex alloys such as 16-25-6.

Brazing and Soldering of Nickel, Monel and Inconel

See abstract on p. 235.

Bonding of Titanium Carbide with Nickel

W. J. ENGE: 'Bonding Investigation of Titanium Carbide with Various Elements.' *Nat. Advisory Committee for Aeronautics, Tech. Note* 2187, Sept., 1950; 15 pp.

In connexion with the study of ceramals as high-temperature materials for use in aircraft turbine components, a study has been made, at the Lewis Flight Propulsion Laboratory, of the bonding of titanium carbide with various elements. Although the conditions obtaining were not strictly analogous to those prevailing in the sintering of a body of intimately mixed powder constituents, the reactions between the powdered elements and the solid titanium carbide are considered to be characteristically indicative of those occurring between intimately mixed discrete particles, as in a sintered body. It was thus possible to determine, as a secondary object of the investigation, the nature of the mechanism of bonding.

Titanium carbide was selected on account of its relatively high resistance to thermal shock, and the elements chosen were aluminium, beryllium, chromium, cobalt, niobium, gold, iron, lead, magnesium, manganese, nickel, platinum, silicon, titanium and vanadium. These were individually fused on solid, high-density titanium carbide, at minimum fusion temperatures, in a helium atmosphere, and at atmospheric pressure.

Only nickel, cobalt, chromium and silicon produced bonds: the most extensive bonds were those made with nickel and cobalt. Larger amounts of titanium carbide were present in the nickel/carbide and cobalt/carbide interfaces than in the other samples, and metallographic examination of the bonded materials showed small angular-shaped precipitates in the nickel- and cobalt-rich areas, an observation which is considered to substantiate the solubility (probably only of limited extent) of titanium carbide in these two metals. The silicon/titanium-carbide specimens were somewhat more fragile than the other bonded samples.

The results lead to the conclusion that employment of nickel and cobalt, and possibly also of chromium, in this application, is promising.

Nickel-, Inconel- and Stainless Steel-Clad Molybdenum for High-Temperature Service

W. L. BRUCKART and R. I. JAFFEE: 'Cladding of Molybdenum for Service in Air at Elevated Temperatures.' *Amer. Soc. Metals, Preprint* 18, Oct., 1951; 23 pp.

Creep-rupture tests on molybdenum at 1800° and 2000°F. (980° and 1090°C.), made in vacuum, have shown that, in this temperature range, molybdenum is stronger than any other wrought structural material. The use of molybdenum for high-temperature service is, however, precluded by the fact that the metal has poor oxidation-resistance: limiting service temperatures for bare molybdenum in air are of the order of 930°F. (500°C.).

A considerable amount of study has already been carried out on methods which may be used for protection, including exploration of the usefulness of

(1) coatings of molybdenum disilicide, (2) oxide coatings, (3) alloying with other metals, and (4) cladding. Coatings of types (1) and (2), while in some cases conferring a good degree of protection from oxidation, are limited to applications in which the material is not subjected to deformation or impact. Method (2) is currently under investigation by several laboratories, since it is recognized that the development of an oxidation-resistant strong molybdenum alloy would form an ideal solution to the problem. No reports have yet been published indicating attainment of this ideal.

The present paper is concerned solely with the use of cladding as a means of protection, and the results are believed to demonstrate that the useful service-temperature range of molybdenum in air can be raised to 2000°F. (1095°C.) by cladding with nickel or Inconel.

The investigation comprised creep tests at 1800°F. (980°C.), and study of oxidation-resistance, diffusion of basis and cladding material, and recrystallization behaviour, at 1800°, 2000°, 2200°F. (980°, 1095° and 1205°C.). The effects of variations in thickness of cladding, fabrication temperature, core metal, and type of cladding were examined: methods of protecting cut edges and of joining clad sheets were also studied. The cladding materials for which data are reported were nickel, Inconel and nickel-chromium stainless steel.

In addition to the high-temperature tests, the properties of the core materials and the clad composites were examined by means of room-temperature tensile tests, and determination of bend ductility and bond strength (nickel-clad material only). Thermal-shock resistance was also examined, on all three types of clad material, as a supplement to the bond-shear-strength tests.

The general conclusion from the series of tests, full details of which are recorded in the paper, is that cladding with nickel is a practical method of utilizing the superior high-temperature strength of molybdenum.

Inconel cladding has some advantages over nickel, e.g., better resistance to oxidation, and superior fabrication characteristics, but the poorer bond strength of Inconel to molybdenum is considered to outweigh any advantages. Limiting service temperatures for the two clad materials are estimated. Life at 2000°F. (1095°C.) is estimated as at least 500 hours for both types of clad material. At 1800°F. (980°C.) a life of over 1800 hours may be expected with Inconel-clad molybdenum, and for nickel-clad molybdenum the estimate would be about 1850 hours. It is predicted that at 2200°F. (1205°C.) neither nickel- nor Inconel-clad molybdenum can withstand more than 250 hours in air atmosphere.

It was observed that clad powder-produced molybdenum showed higher creep strength than clad material in which arc-cast molybdenum was used: this conclusion awaits confirmation.

Satisfactory joining and edge protection of clad molybdenum can be effected by the use of nickel or Hastelloy B filler metal, and argon-arc or oxy-acetylene braze-welding procedures.

Stainless Steel Tubing: Mechanical and Physical Properties

'High-Temperature Properties of Stainless Steel Tubing.' *Materials and Methods*, 1951, vol. 34, Sept., p. 113.

Data sheet giving properties typical of steel tubing of the following types of material:—304, 309, 330, 310, 316, 317, 321, 347, 430 and 443.

The information tabulated relates to coefficient of thermal expansion over various ranges, scaling temperatures, short-time and creep properties at various temperatures, structural stability at elevated temperatures, melting points, thermal conductivity, and specific heat.

Ferrite Formation in the Sensitizing Range in Austenitic Steels

E. J. DULIS and G. V. SMITH: 'Ferrite Formation Associated with Carbide Precipitation in 18-Cr/8-Ni Austenitic Stainless Steel.' *Amer. Soc. Metals, Preprint* 14, Oct., 1951; 12 pp.

Relatively high ferromagnetism was observed in a sample of 18-8 chromium-nickel steel which had been in oil-refinery service for 10 years, in a temperature range reported to be normally within the limits 1050°–1100°F. (565°–595°C.), with occasional rise to 1200°F. (650°C.). This specimen was examined, in comparison with a sample of 18-8 which showed only slight ferromagnetism after 3,000 hours at 1100°F. (595°C.).

The authors preface their report with a good review of the earlier literature on ferrite formation associated with carbide precipitation.

Examination comprised microscopic study, determination of hardness and of magnetic permeability, and X-ray-diffraction measurement. The results, reported in detail, lead to the conclusion that, during heating, the ferrite present starts to transform to austenite at about 900°F. (480°C.), whereas the reverse transformation from austenite to ferrite (martensite) does not begin until the steel is cooled below about 500°F. (260°C.). The transformation is essentially reversible, with a hysteresis of some 600°F. (333°C.) if the heating temperature does not exceed about 1200°–1300°F. (650°–705°C.).

The observations made are considered to provide strong support to a theory proposed by BUEHL *et al.* (*Trans. Amer. Inst. Min. Met. Eng.*, 1940, vol. 140, pp. 368-87) that ferrite formation associated with carbide precipitation in austenitic chromium-nickel steels occurs during cooling, rather than at the temperature at which the carbide precipitates. Buehl suggests that the ferrite forms as a result of lattice strains surrounding the precipitated carbides, but the present authors consider that the alloy depletion, i.e., lower chromium and carbon content surrounding a carbide particle, cannot be ignored, and that it may even be a more important factor. If this were not so 'induced' ferrite should be observed in other austenitic steels, such as 25-20 chromium-nickel, from which it is actually absent. Such a line of reasoning would suggest that the lower chromium content of the highly ferro-

magnetic steel was responsible for the extraordinarily large amount of the ferrite observed after service (approximately 20 per cent.), as compared with the amount found in the other steel, which was too small to be detected microscopically.

Stress-Corrosion Cracking in Alkaline Solutions: Reference Data

H. W. SCHMIDT, P. J. GEGNER, G. HEINEMANN, C. F. POGACAR and E. H. WYCHE: 'Stress Corrosion Cracking in Alkaline Solutions.' Report issued by Technical Practices Committee 5 C: Sub-Surface Corrosion by Alkaline Solutions.

N.A.C.E. Technical Practices Committee Publication 51-3.

Corrosion, 1951, vol. 7, Sept., pp. 295-302.

It is pointed out that 'stress-corrosion cracking in alkaline solutions' is a more correct designation of the type of failure under consideration than the very commonly used term 'caustic embrittlement', since the effect is not intrinsically an embrittlement of the metal.

With regard to the theory and background of the subject, the Committee directs attention to the paper by HARWOOD on stress-corrosion cracking of metals in general, presented to the National Association of Corrosion Engineers in 1950 (*ibid.*, 1950, vol. 6, pp. 249-59, 290-307), and to the treatise on stress-corrosion in mild steel by WABER and MACDONALD (published by Corrosion Publishing Company, Pittsburgh, Pa.). Theories of stress-corrosion cracking discussed by Harwood are briefly summarized in the present review.

The major part of the report is based on replies to a questionnaire sent out to representative plants in the chemical and process industries. The information so received is presented in two tables embodying details of type of equipment to which the experience relates, type of construction, materials of construction, concentration of caustic involved in the service described, temperature of operation, time to failure, and general supplementary remarks. Most of the large number of cases reported relate to caustic soda: the data are arranged in order of increasing concentration of sodium hydroxide. Materials of construction used in one or several ranges of concentration include steels of various types (including specific reference to 3½ and 5 per cent. nickel steels), nickel and nickel-clad steel, and irons of various grades.

Some information was also provided by the plants with regard to behaviour of materials in contact with alkaline solutions other than sodium hydroxide. These data are separately listed: they include reference to about a dozen alkaline solutions of simple or complex types, and the materials of construction mentioned cover various grades of nickel-chromium stainless steel, stainless-clad steel, and copper-base alloys.

From the information supplied, the Committee has also prepared a graph showing temperature and sodium-hydroxide concentration in relation to susceptibility to failure by cracking.

The influence of operations such as welding, bending, rolling, etc., on the degree of stress present in the materials as put into service, is also considered, and the value of stress-relief treatments is indicated.

The final section of the report contains a succinct critical discussion of corrective measures suggested by contributors to the questionnaire-information service. These measures are considered in three groups: (1) those effecting a *decrease in stress level* (modified design or mode of operation of plant; stress-relief treatment); (2) those effecting a *decrease in temperature* (e.g., by change in design), and (3) *change in materials*.

In connexion with remedial method (3), it is reported that 'it seemed to be the consensus of opinion that to eliminate stress-corrosion cracking in steel a change to nickel or Monel, or nickel-clad steel, was indicated. The actual selection from the three metals will be determined by the economics involved'. Some cases of failure of nickel-clad welds recorded are believed to have been due to faulty welding procedure; improved welding and inspection techniques are reported to have ensured sound welds. Some success has also been achieved by metal spraying of welded surfaces with nickel.

In the light of the information provided, the Committee suggests further lines of research:— various methods of stress-relieving; the effectiveness of shot peening as a mode of stress-relieving; the influence of cathodic protection, and the extent to which protective coatings may prove effective. It is also proposed that the relation of impurities in steel and incidence of stress-corrosion cracking in alkaline solutions should be studied.

Resistance of Nickel and Nickel Alloys to Corrosion by Boron Trifluoride

F. HUDSWELL, J. S. NAIRN and K. L. WILKINSON: 'Corrosion Experiments with Gaseous Boron Trifluoride.' *Jnl. Applied Chemistry*, 1951, vol. 1, Aug., pp. 333-6.

Increasing demand for boron trifluoride of a very high degree of purity has necessitated investigation of the resistance, to this gas, of materials commonly used in neutron counters in particular, and in chemical plant in general.

Boron trifluoride is an extremely reactive gas. It is rapidly attacked by traces of moisture, giving hydroxyfluoboric acids and hydrogen fluoride as products of the reaction: the reactivity of hydrogen fluoride must therefore also be considered if moisture is present.

In the experiments reported conditions were controlled to avoid any reactions other than those which might occur between dry boron trifluoride of high purity and the materials under test. Metals and other materials were thoroughly cleaned and dried, and the tests were made in all-glass apparatus which had been fully evacuated and dried. Experimental conditions are fully described.

Reactions of the specimens were determined, at various temperatures, by bringing them into contact with the gas at an original fixed pressure of about 25 cm. of mercury. The extent of the reaction, if any, was measured by alteration of the gas pressure over the sample. Temperatures of exposure:—for all specimens (metallic and non-metallic) 25°C., 50°C.

and 80°C.: for metallic specimens only 200°C. Time of exposure ranged, for metallic specimens, from 12, 14, 21 or 32 days at 25°C. (varied according to the material under test) to 5 hours at 200°C.

Many of the materials examined showed high resistance to attack, and the results of the tests indicate that the following metals and alloys can safely be used in apparatus handling dry boron trifluoride:—stainless steel, mild steel, copper, nickel, Monel, brass, aluminium, and the more noble metals, e.g., gold, silver, platinum. Pyrex glass is suitable up to about 200°C., and certain cement and plastic materials showed satisfactory resistance up to 80°C. Other materials in the non-metallic group showed wide variation in behaviour.

Resistance of Nickel-containing Materials to Phenol

'Materials of Construction vs. Phenol.' *Chemical Engineering*, 1951, vol. 58, Aug., pp. 222, 224, 226, 228.

This section of the Corrosion Forum comprises short summaries of the behaviour of the following materials in contact with phenol:—nickel and nickel alloys, carbon and graphite, Worthite, Hastelloy alloys, high-silicon irons, Durimet 20, aluminium, Chlorimet alloys, glass, non-metallic coatings, stainless steel, silicones, cements, iron and steel, tantalum, rubber, lead.

Nickel and Nickel Alloys are very widely used for storage, handling, distillation and condensation of phenol, in order to maintain maximum purity of product and freedom from discoloration. Nickel has become established as the standard material for tanks and pipelines.

Inconel and Monel have approximately the same degree of corrosion resistance as nickel, but for long-time storage of a high-purity product nickel is to be preferred.

Worthite is practically immune from attack by phenol under all conditions, and pumps and valves of this material are used both in manufacture and in the industries in which phenol-containing products are handled. Worthite pumps also show excellent resistance to the erosive action of phenol-lime slurry solutions.

Hastelloy Alloys. Solutions of pure phenol are claimed to have essentially no effect on the Hastelloy alloys, regardless of temperature or concentration: typical applications of grades B and D are quoted, and some spool-corrosion test data are recorded, showing the behaviour of Hastelloy alloys in various phenol-containing mixtures.

Durimet 20 shows excellent resistance to phenol at all temperatures and concentrations normally encountered. It is also suitable when sulphur compounds are present with the phenol, and can be used in contact with hot phenol vapours at temperatures up to about 600°F. (315°C.).

Chlorimet Alloys also are practically immune from corrosion by phenol, at all temperatures and concentrations, and the presence of sulphur does not lower their corrosion-resisting quality. They are not, however, extensively used in this connexion, due to the good degree of corrosion-resistance offered by less expensive materials such as Durimet 20, and the nickel-chromium stainless steels.

Stainless Steels. 18-8 steels of the 304 and 316 types are satisfactory in many phases of the refining of phenol, but solutions containing appreciable amounts of water may cause pitting. In such cases the 316 grade is the more suitable. Straight-chromium steels of the 410, 430, as well as the 304 and 316 austenitic grades, are unattacked by the non-aqueous liquid at low temperatures, and nickel-chromium steel equipment will safely handle either crude or chemically pure phenol at all temperatures. Type 316 is to be preferred for exposure to hot vapours, and in presence of crystals. Certain sterilizing solutions containing carbolic acid tend to cause pitting of Type 304 steel if exposure is prolonged.

Resistance of Nickel-containing Materials to Fertilizers and Other Corrodents: T.V.A. Tests

L. D. YATES: 'Corrosion Tests of Metals and Ceramics.' *Tennessee Valley Authority, Chemical Engineering Report No.* 9, 1951; 56 pp.

The Report is one of a series describing the chemical-engineering activities of the T.V.A.: it contains results of some of the corrosion tests made in the course of development of processes for production of fertilizers, and the utilization of the natural resources of the Tennessee Valley.

The tests recorded include exposures of metallic materials and of ceramics, against compounds of phosphorus, nitrogen, sulphur, aluminium and magnesium, in both plant and pilot-plant equipment, and in the laboratory. Methods adopted and test set-ups are described and illustrated.

The Report is of a reference nature, which does not permit detailed abstraction, but the scope of the information obtainable from the original is indicated below, by giving (*a*) the nature of the corrosives against which the tests were made, and (*b*) the types of material exposed in some or all of the tests.

(*a*) *Corrosives*:

Phosphoric acid (both electric-furnace acid from the T.V.A. plants and C.P. acid).

Vapour containing phosphoric acid and some fluorine (probably present as hydrogen fluoride), in a gas stream of which the principal constituent was nitrogen.

Phosphoric-acid solutions containing other mineral acids and salts.

Ammonium-phosphate solutions.

Electrostatic phosphorus precipitator seal oil, with and without phosphorus-pentoxide contamination.

Sulphuric acid, with and without other materials.

Aluminium sulphate.

Nitric acid.

Ammonium nitrate, with and without other materials.

Copper-ammonium-acetate solutions.

Various compounds of fluorine.

Magnesium-chloride solutions containing small amounts of hydrochloric acid.

(*b*) *Materials tested*:

Stainless steels (austenitic nickel-chromium and straight-chromium types).

Aluminium and aluminium alloys.

Cast irons (plain and high-alloy types).

Copper and copper-base alloys (including simple and

complex brasses and bronzes, and copper-nickel types).

Complex 'special' corrosion-resisting materials, e.g., Carpenter 20, Croloy, Durimet, Durichlor, Duraloy.

Lead.

Mild Steel.

Nickel and high-nickel alloys, including Monel, K and S Monels, Inconel, 80-20 nickel-chromium, Illium, La Bour R-55, Chlorimet 2, and the Hastelloy Alloys A, B, C and D.

Precious metals (gold, silver, platinum).

Tantalum.

Ceramic materials of various types.

Nickel and Monel Equipment in Production of Detergents

'Monsanto at Newport.' *Chemistry and Industry*, 1951, Sept. 8, pp. 755-7.

Description of the extensive Monsanto plant, specially designed to manufacture products which Britain has up till now been obliged to import.

A large plant for the manufacture of Santomerse detergent came into operation in 1949, followed, at fairly close intervals, by other units. The present layout, completed in 1950, represents stage one of the final plant: it is designed for production of styrene plastics, detergents, oil additives, preservatives, fungicides and the Arochlors, (a group of substances employed as plasticizers in plastics, paints and varnishes, and also in transformer oils).

In the course of a brief description of some outstanding features of the processes already in operation, special attention is directed to the Santomerse plant (the largest section of the factory), which is engaged in production of a water- and oil-soluble detergent having a wide range of applications. The process involved in manufacture of this substance is, in various stages, such as to impose severely corrosive conditions, and an interesting feature of the plant is stated to be the number of corrosion-resisting materials employed in it. Some of the vessels are of solid nickel, others are lined with silver or with enamel, and still others require the use of Monel. (It should be noted that, in the original, Monel is referred to as a 'nickel-chromium alloy': this should read 'nickel-copper' alloy).

Stainless Steel for Handling Lubricating Oils

D. W. SAWYER: 'Catalytic Effect of Several Metals on the Oxidation of Lubricating Oils.' *Amer. Soc. Mechanical Engineers, Paper* 51–*SA*–3, June, 1951; 7 pp.

During service, mineral oils deteriorate due to reaction with the moisture and the oxygen in the air. The rate of such reactions is much increased by heat, and as the temperature rises the oil becomes increasingly susceptible to the catalytic influence of metals, which further accelerates deterioration.

Compounds produced in the oils by such oxidation, or the presence of moisture entrained in the oil, may corrode the metals, and is frequently a cause of clogged oil lines, filters and screens, with resulting failure of bearings arising from absence of lubricant. Metals which do not catalyze such reactions would therefore be expected to be more suitable than the more catalytic metals for fabrication of parts in contact with oil.

As a result of reports issued by other investigators, and of preliminary tests carried out in the Aluminum Research Laboratories, the Aluminum Company of America instituted a systematic investigation of the behaviour of commercial metals and alloys in contact with lubricating oils. The oils used comprised three types broadly representative of those obtainable from Pennsylvania, Mid-American Continent, and Gulf Coast crudes, and five other samples typical, respectively, of inhibited aviation motor oil, straight uncompounded motor oil, heavy-duty machinery circulating oil, and inhibited steam-turbine lubricating oils (*a*) oxidation-stabilized, and (*b*) oxidation- and corrosion-stabilized. The following materials were tested for their reaction with the oils: typical aluminium alloys, copper, lead, low-carbon steel, 18-8 chromium-nickel steel, tinplate, zinc. A few additional exploratory tests were carried out with pure magnesium, magnesium alloy and a 68-32 brass.

A detailed account is given of the characteristics of the oils, the equipment and testing technique used, and the behaviour of the materials under various conditions of time and temperature of exposure.

The results show that aluminium-base alloys and nickel-chromium stainless steel have very little or no catalytic effect on oxidation of the oils. Copper and low-carbon steels, however, markedly accelerate oxidation.

Copper, lead and zinc were, in general, corroded to a much greater degree than were any of the other metals, and in a number of cases low-carbon steel, magnesium, magnesium alloy and tinplate were less resistant to corrosion than the other materials tested.

The catalytic effect of the metals which showed reaction was much increased by rise in temperature, and, as a rule, the increase in catalytic effect was paralleled by more severe corrosion attack. The aluminium-base alloys and the stainless steel showed no appreciable corrosion.

Determination of Hydrogen in Nickel-Alloy Steels

See abstract on p. 241.

Determination of Cobalt in Nickel-containing Materials

See abstract on p. 234.

Attention is drawn to the fact that many of the names of materials mentioned in The Nickel Bulletin are *Registered Trade Marks.*

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WESTMINSTER, LONDON, S.W.I